BULLETIN OF THE ACADEMY
OF SCIENCES U.S.S.R.
VOL. 4 NO. 3 - 1955

A. V. DUMANSKY, Corresponding Member of the Academy of Sciences of the USSR and Active Member of the Academy of Sciences of the Ukrainian SSR

Dear Anton Vladimirovich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, congratulate you on the attainment of the age of seventy-five years.

You have devoted the whole of your creative life to work on colloid chemistry, of which you are founder, propagandist, and successful exponent. You have created the Soviet school of colloid chemists. You are the originator and permanent editor of the Colloid Journal.

Your scientific, organizing, and teaching work has made a large and valuable contribution to the development of Soviet science.

We hope that there still lie before you many years of vigor, of health, and of fruitful labors devoted to the welfare of our beloved Fatherland.

Note: The photograph accompanying this salutation has not been reproduced in this translation because of the limitations of the printing process used. Publisher.

BLANK
PAGE

EXPERIMENTAL DETERMINATION OF THE SEQUENCE OF SUCCESSIVE ELEMENTARY REACTIONS OF ATOMS AND RADICALS

L. I. Avramenko and R. V. Kolesnikova

Detailed study of mechanisms of chemical reactions proceeding via intermediate stages in which radicals and atoms take part is important not only for the understanding of the actual process of chemical change, but also for the solution of practical problems. The existing concepts of the mechanism of chemical changes in which radicals take part, e.g. oxidative processes, are inadequate. Thus, various views have been expressed in the literature [1-9] on the processes of peroxide and aldehyde formation in the oxidation of hydrocarbons. Some authors consider that peroxides are primary oxidation products, and alcohols and aldehydes are secondary products; other authors consider that peroxides and aldehydes are formed simultaneously and independently.

In itself, therefore, the concept of a reaction proceeding via atom and radical formation is insufficient to enable the actual mechanism of a complex reaction to be understood and to be described quantitatively. It is necessary to have experimental proof of the existence of one or another kind of radicals in the reaction zone. Moreover, it is necessary to know what reactions can be given by the radicals and what the rate constants of these reactions are. However, many difficulties lie in the way of an extensive study of the elementary reactions of atoms and radicals. These difficulties arise from various causes, one of the most important being the shortness of the lives of atoms and radicals. This last circumstance makes it necessary to use special methods for the study of the reactions of atoms and radicals.

In our investigations of the elementary reactions of oxygen and hydrogen atoms, we have found a method that enables us to obtain information about the elementary reactions of the atoms from an examination of the ultimate reaction products. It is much easier to make measurements on the ultimate products, rather than the intermediates, but in order to obtain information about actual elementary reactions it is first necessary to know the order in which the reactions occur, since a given ultimate product can often be obtained either by a single elementary act, or by several successive elementary processes.

We propose a method that enables the sequence of the elementary reactions to be determined experimentally from the behavior of the ultimate reaction products. This method is illustrated by the reactions of atomic oxygen with various substances. The applicability of the method is not confined solely to the reactions of oxygen atoms, but may be extended to atoms and radicals of all kinds.

The apparatus in which the experiments were carried out is shown diagrammatically in Fig. 1. The whole of the apparatus was constructed of molybdenum glass. Atomic oxygen could be prepared in the apparatus either from water vapor or from molecular oxygen, a stream of the substance being passed through the discharge tube 2, a conical nozzle 1 (length 30 mm; diameter 1.5 mm at the discharge-tube end and 5 mm at the reaction-vessel end), and the reaction vessel 3. For a linear streaming velocity of 300-800 cm per second this method of construction enabled fuel to be passed into the reaction vessel over a wide range of concentrations without the slightest signs of diffusion of fuel into the discharge. Any such diffusion was readily detected visually by change in the color of the discharge at the nozzle. Fuel was supplied through the capillary 4, which was fused into the reaction vessel 3. The fuel supply was regulated by the valve 5, which was found to be very convenient for the regulation of a gas stream, being equivalent to a wholerange of capillaries varying in diameter. The combustible gases were kept in a gas holder, and were passed into the calibrated flask 14 before the experiment. The consumption of gas was measured with the aid of the flask 14 and the manometer 15. Reaction products that could be condensed with liquid air were collected in the detachable trap 10. Carbon monoxide was determined by oxidation over Hopcalite in the tube 12, through which the stream passed after leaving the trap 10; CO_2 was then frozen out in the trap 18. The interchangeable joints 6, 7, 8, and 9 were used for the introduction of oxygen (or any other gas required) into various parts of the reaction zone. The vessel 11 served for the taking and separation of samples of gaseous products; they were taken from the trap 10, and collected by a freezing-out process.

It should be noted that in such an apparatus, atomic oxygen may be prepared from water vapor without any appreciable admixture of molecular oxygen [10]. That this is so follows from the fact that the addition of oxygen molecules in the reaction zone results in the appearance of new products or in increase in the amount of

the products formed when no addition of oxygen is made. This indicates that radicals are present in the reaction zone which yield these products by reaction with molecular oxygen. The utilization of this fact is of great importance in our method for determining the order in which elementary reactions occur.

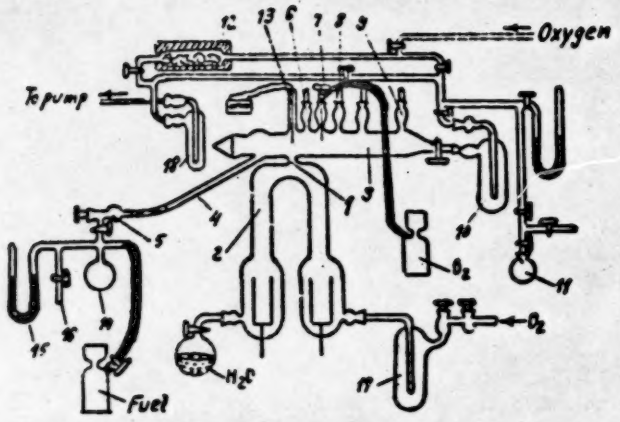


Fig. 1. Diagram of apparatus: 1-conical nozzle; 2-discharge tube; 3- reaction vessel; 4-capillary; 5-valve; 6, 7, 8, and 9-interchangeable joints, through which additions are made; 10- detachable trap; 11-transfer vessel; 12-tube containing Hopcalite; 13 - thermocouple; 14 - calibrated flask; 15-manometer; 16- side tube required when liquid fuels are used; 17 - trap for drying gas (O_2 or H_2); 18- detachable trap

In order to avoid confusion in terminology it is necessary to give some definitions. A primary reaction is a reaction of an original active center (oxygen atom) with an original fuel molecule, or the reaction of an original radical with an oxygen molecule. Quadratic reactions are reactions between primary products (molecules and radicals) and the original active center (oxygen atom). Cubic reactions are reactions between quadratic reaction products (molecules and radicals) and the original active center. Secondary reactions are reactions between primary (not to be confused with "original") radicals obtained in primary reactions and molecular compounds having no free valencies, and also the decomposition reactions of primary radicals and molecules.

Hence, primary and secondary products are formed by a single act of interaction with the original active center, whereas quadratic reactions require two acts, and cubic three acts, of interaction with the original active center.

Concentrations will be represented as follows: original substance A, oxygen atoms O, primary product B, quadratic product D, cubic product F, secondary product C, and various radicals R. The corresponding reaction constants will be denoted by K with various subscripts and superscripts. The general scheme can be represented as follows:

$$O + A \xrightarrow{K_1} \begin{cases} B & K_1' \\ B_1 + R & K_1'' \end{cases} \quad \text{primary}$$

$$R + O_2 \xrightarrow{K_2} C + R_1 \qquad K_2 \quad \text{secondary}$$

$$O + B \text{ (or } C) \xrightarrow{K_4} \begin{cases} D & K_4' \\ D_1 + R_2 & K_4'' \\ F & K_4''' \end{cases} \quad \text{quadratic}$$

$$O + D \xrightarrow{K_3} \begin{cases} F_1 + R_3 & K_3' \\ O + O + M \xrightarrow{K_M} O_2 + M \\ O + \text{wall} \xrightarrow{K_5} \end{cases} \quad \text{cubic}$$

On the basis of this general scheme the following kinetic equations can be written for A, B, C, D, E, and O:

$$\frac{dA}{dt} = -K_1(A)(O)$$

$$\frac{dB}{dt} = K_1^1(A)(O) - K_4(B)(O)$$

$$\frac{dC}{dt} = K_2^1(R)(O_2) - K_4(C)(O)$$

$$\frac{dD}{dt} = K_4^1(B)(O) - K_3(D)(O)$$

$$\frac{dF}{dt} = K_3^1(D)(O)$$

$$-\frac{d(O)}{dt} = K_1(O)(A) + K_4(O)(B) + K_3(O)(D) + K_M(O)^2 + K_0(O)$$

By the simultaneous solution of these equations with application of the limiting conditions [when $A = A_0$, $(O) = (O)_0$ and $B = D = C = F = 0$;] and when $A = A_f$, $B = B_f$, $D = D_f$, $F = F_f$, $C = C_f$, and $(O)_f = 0$ we obtain expressions for the quantities of interest to us, B, C, D, F, and O, as functions of A.

For the primary product B reacting with atomic oxygen an expression of the following form is obtained:

$$B_f = \frac{K_1^1}{K_1 - K_4} A_0 \left(a^{\frac{K_4}{K_1}} - a \right). \tag{1}$$

in which B_f denotes the final concentration of the primary product (the concentration at the end of the reaction zone), A_0 denotes the initial concentration of the original substance, and a denotes the ratio A_f/A_0. For the secondary product C an expression similar to (1) is obtained:

$$C_f = \frac{K_1^1 K_2^1}{K_2(K_1 - K_4)} A_0 \left(a^{\frac{K_4}{K_1}} - a \right). \tag{2}$$

in which C_f is the final concentration of the secondary product.

For the quadratic product D an expression of the following form is obtained:

$$D_f = \frac{K_4^1 K_1^1}{K_1 - K_4} A_0 \left[\left(\frac{1}{K_4 - K_3} - \frac{1}{K_1 - K_3} \right) a^{\frac{K_3}{K_1}} - \frac{1}{K_4 - K_3} a^{\frac{K_4}{K_1}} + \frac{a}{K_1 - K_3} \right]. \tag{3}$$

in which D_f is the final concentration of the quadratic product.

For the cubic product F, which does not react further with atomic oxygen, an expression of the following form is obtained:

$$F_f = \frac{K_4^1 K_1^1}{K_4 - K_1} A_0 \left[\left(\frac{1}{K_4 - K_3} - \frac{1}{K_1 - K_3} \right) a^{\frac{K_3}{K_1}} - 1 \right) - \frac{K_3}{K_4(K_4 - K_3)} \left(a^{\frac{K_4}{K_1}} - 1 \right) + \frac{K_3}{K_1(K_1 - K_3)} (a - 1) \right]. \tag{4}$$

in which F_f is the final concentration of the cubic product.

The relation between a and A is given by the formula:

$$A_0 = \frac{-\frac{K_3}{K_M} + \left[(O)_0 + \frac{K_3}{K_M} \right] a^{\frac{K_M}{K_1}}}{(a+b+c)a^{\frac{K_M}{K_1}} - a a^{\frac{K_4}{K_1}} - b a^{\frac{K_3}{K_1}} - c a}. \tag{5}$$

in which $(O)_0$ is the initial concentration of atomic oxygen;

$$a = \frac{K_1}{K_1 - K_M} + \frac{K_1 K_4}{(K_4 - K_1)(K_1 - K_M)} - \frac{K_1 K_2 K_4}{(K_4 - K_1)(K_1 - K_3)(K_1 - K_M)};$$

$$b = \frac{K_1 K_2 K_4}{(K_4 - K_1)(K_4 - K_2)(K_4 - K_M)} - \frac{K_1 K_4}{(K_4 - K_1)(K_4 - K_M)};$$

$$c = \frac{K_1 K_2 K_4}{(K_4 - K_1)(K_1 - K_2)(K_2 - K_M)} - \frac{K_1 K_2 K_4}{(K_4 - K_1)(K_4 - K_2)(K_2 - K_M)};$$

The physical significance of a is such that it can vary from zero to unity. When the constants K_1, K_2, K_4, K_M, and K_0 are given definite values, values of A_0 can be found for various values of a.

As an example we will make calculations for ratios of constants that are probable for the reaction of oxygen atoms with the ethane molecule, namely:

$$\frac{K_4}{K_1} = 10; \quad \frac{K_2}{K_1} = 0.5; \quad \frac{K_M}{K_1} = 0.05; \quad \frac{K_2}{K_M} = 6.5 \cdot 10^{15}; \quad (O)_0 = 8 \cdot 10^{14}.$$

The constants K_M and K_0 are known [10]. We then obtain: $a = 1$, $b = -0.105$ and $c = 2.34$. Substituting all the numerical values of constants in Equation 5, we obtain:

$$A_0 = \frac{6.5 \cdot 10^{15} - 7.3 \cdot 10^{15} a^{0.05}}{a - 0.105 a^{15} - 3.235 a^{0.85} + 2.34 a^{0.5}} \qquad (6)$$

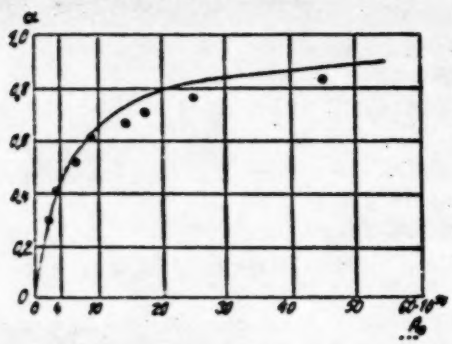


Fig. 2. Curve for the dependence of a on A_0 (the continuous line represents the calculated relation for ethane, and the points represent the experimental values for ethane)

Fig. 2 represents the relation between a and A_0 according to Equation 6. For other ratios of the constants K_1, K_4, and K_2, the curves obtained are similar in form to that in Fig. 2.

By a suitable choice of constants the relation between a and A_0 can be determined for the reaction of oxygen atoms with any other molecule. By the use of the known dependence of a on A_0, the relation of B_f, D_f, and F_f to A_0 can be represented graphically.

Fig. 3 gives the curves for the dependence of B_f, D_f, and F_f on A_0. These curves have been constructed with the aid of Equations 1, 3, and 4 and the calculated relation of a to A_0 for ethane, and it was assumed the $K_4' = K_4$ and $K_1' = K_1$. The equality of these constants occurs when the original substance forms only one primary product, which then forms only one quadratic product.

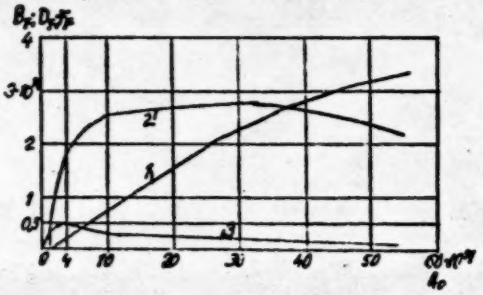


Fig. 3. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane (the calculated value for a for ethane is used): 1 - primary product B_f; 2 - quadratic product D_f; 3 - cubic product F_f

In Fig. 3 the differences between the primary, quadratic, and cubic reaction products are clearly seen: the curve for the cubic product bends over toward the maximum value at a lower value of A_0 than the curve for the quadratic product, which itself bends over at a lower value of A_0 than the curve for the primary product. Also, the curves for the cubic and quadratic products have maxima but the curve for the primary product has only a limiting value; the value of the maximum on the curve for the quadratic product is less than half of that of the limiting value for the primary product.

This picture is readily understood when physical aspects of the phenomena occurring under the conditions of the experiment are examined. When the concentration of the original substance is low, atomic oxygen may react not only with this substance, but also with primary and quadratic reaction products. As the concentration of the original substance is increased at a constant concentration of atomic oxygen, an increasing proportion of the oxygen atoms will react only with the original substance and a diminishing proportion will react with reaction products. Finally, at sufficiently high concentrations of the original substance, oxygen atoms will react only with this substance and only the primary product will be formed. Further increase in A_0 will no longer result in a rise in the final concentration of the primary product, since all of the oxygen atoms produced will participate only in the

primary reaction. Hence, at very high fuel concentrations, the amount of oxygen-containing primary product formed will attain its limiting value. This limiting value should be equivalent to the amount of atomic oxygen passed into the vessel during the same period of time.

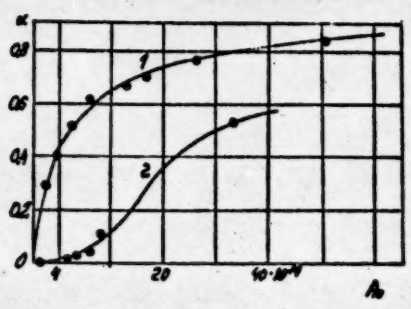


Fig. 4. Experimental curves for the dependence of α on A_0: 1- for ethane; 2- for formaldehyde

Fig. 5. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane (the experimentally found value of a for ethane is used): 1- primary product; 2- quadratic product; 3- cubic product

It will be evident that the amount of quadratic product at its maximum cannot be more than half the amount of primary product at its limiting value, and the amount of cubic product cannot attain more than one-third of the limiting value for the primary product, for the quadratic product requires two oxygen atoms for its formation, and the cubic product requires three.

The value of α and its relation to A_0 can be measured experimentally under the conditions we have employed. These measurements were carried out for a few substances. The results of such measurements with ethane as an example of fuels that do not react readily (Curve 1) and formaldehyde as an example of fuels that react readily (Curve 2) are represented graphically in Fig. 4.

Comparison of Figures 2 and 4 shows that curves for the dependence of α on A_0 obtained by experiment and by calculation are very close together. The points lying along the calculated curve in Fig. 2 represent the experimental results. The satisfactory accord between experimental and calculated curves indicates that the ratios of the reaction-rate constants K_1, K_3, and K_4 that we have assumed for ethane in the calculations are close to their true values.

Fig. 5 shows curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane. These curves are constructed from Equations 1, 3, and 4, the values taken for α being those obtained experimentally. In the construction of the curves it was assumed that $K_1^i = K_1$ and $K_4^i = K_4$. Fig. 5 shows the difference between the primary products and the quadratic and cubic products.

A mathematical and graphical analysis that we have carried out for the functions B_f, D_f, and F_f shows that, whatever ratios of K_1, K_4, and K_3 may be assumed, the conclusions concerning the different forms of the functions B_f, D_f, and F_f always hold good. When any particular reaction product is formed not only by a purely primary reaction, nor only by a purely quadratic reaction, but by both primary and quadratic reactions, i.e. by a mixed method, a more complex picture is obtained. The complexity, however, does prevent us from explaining the essence of the phenomenon.

For a mixed product the following expression was obtained;

$$\Sigma_f = \frac{K_1^i}{K_1 - K_4} A_0 \left(\frac{K_4}{K_1} - \alpha + \frac{K_4^i}{K_4 - K_3} \alpha \frac{K_3}{K_1} - \frac{K_4^i}{K_1 - K_3} \alpha \frac{K_3}{K_1} - \frac{K_4^i}{K_4 - K_3} \alpha \frac{K_4}{K_1} + \frac{K_4^i}{K_1 - K_3} \alpha \right). \quad (7)$$

in which Σ_f is the final concentration of the mixed product.

By the use of the known relation of α to A_0, calculated from Equation 6 or determined experimentally, graphs may be constructed for the purely primary, purely quadratic, and mixed reaction products. These are given in Fig. 6 for the reaction of ethane with atomic oxygen, the experimentally found values of α being used. Fig. 6 shows the difference between the curve for the mixed product and those for the purely primary and purely quadratic products: the curve for the mixed product, like that for the quadratic product, bends over at a lower value of A_0 than the curve for the primary product, but with increase in A_0 the curve for the mixed product does not attain a maximum, as the curve for the quadratic product does, but continues to rise linearly, like the curve for the primary product. When the linear part of the curve for the mixed product (Fig. 6, Curve 3) is produced to meet the axis of ordinates (broken line),

the intercept formed corresponds to the value of the maximum final concentration of the quadratic product.

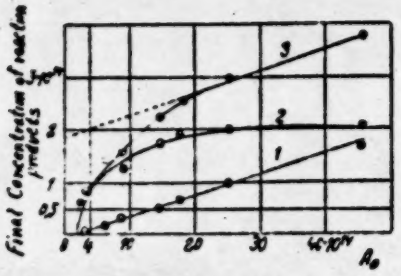


Fig. 6. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and mixed products of the reaction of oxygen atoms with ethane (the experimentally found value of a for ethane is used): 1- purely primary product; 2- purely quadratic product; 3 - mixed product

In this way, from the form of the curves for the final concentrations (and therefore also for the rates of formation of various reaction products) as functions of the initial concentration of the original substance, the primary products can be distinguished from quadratic products, even when mixed reactions occur. We have now shown how the matter stands with respect to primary, quadratic, and cubic products.

A comparison of Equations 1 and 2 shows that the curves for secondary products will be similar in form the curves for primary products. However, a secondary product can appear only when oxygen molecules are present. It is therefore characteristic of a secondary product that it will appear when oxygen molecules are introduced into the reaction zone, so long as its curve is similar in form to that of the primary product.

In order to verify the correctness of the theoretical conclusions, we shall make use of experimental results already published.

Fig. 7 shows graphs for the dependence of the rates of formation (the product of the final concentration, the rate of flow, and the cross-sectional area of the vessel) of ethanol, formaldehyde, CO, and CO_2 on the product of the rate of flow and the concentration of the original ethane. These graphs were constructed from the data in Table 2 of our previous communication [11]. It will be seen that the curves for alcohol and formaldehyde are greatly different in form from those of CO and CO_2. A comparison of the experimental curves (Fig. 7) with the theoretically calculated curves (Figures 3 and 5) indicates that the curves for CO and CO_2 have the form typical for quadratic and cubic products, whereas the curves for alcohol and formaldehyde are typical for primary products.

Actually, it can scarcely be doubted that products such as CO and CO_2 are not formed in the reaction of ethane with oxygen atoms as the result of the primary collision of an oxygen atom with a fuel molecule. However feasible schemes for the formation of these products may be from the point of view of energy changes, it must always be true that for the formation of CO and CO_2 reactions must occur in which at least two atoms of oxygen enter successively into the reaction.

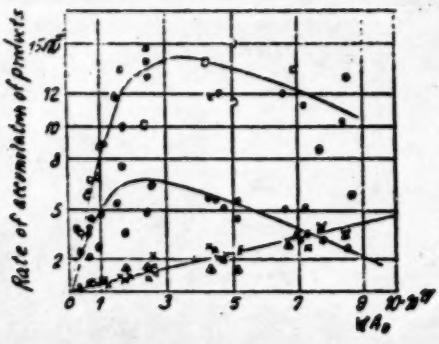


Fig. 7. Curves for the dependence of rates of formation of products of the reaction of atomic oxygen with ethane on the product of the rate of flow and the concentration of original ethane: A – ethanol; x – formaldehyde; o – CO; • – CO_2

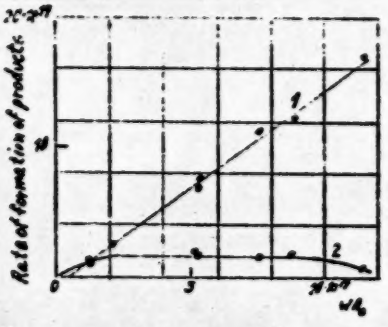


Fig. 8. Curves for the dependence of the rate of formation of reaction products on the product of the rate of flow and the initial concentration of the original formaldehyde: 1- CO; 2. CO_2

Fig. 8 shows curves for the rates of formation of CO and CO_2. It is constructed from data obtained in an investigation of the reaction of atomic oxygen with formaldehyde [12]. In Fig. 8 the difference in the variation of the yields of the primary product CO and the secondary product CO_2 is clearly visible.

The bend in the curve for the quadratic product begins at much lower values of wA_0 than that in the curve for the primary CO. The results of investigations of reactions of atomic oxygen with acetaldehyde [12] and with methane [13] also provide excellent illustrations of the correctness of the method, but the significance of these

results is not confined only to the illustration of the method, for they are of great importance in the study of the mechanism of the formation of oxygen-containing substances by the reactions of oxygen atoms. Moreover, this sequence-determining method enables us to determine the rate constants of the elementary reactions of the original atoms and radicals, and it also enables us to determine the initial concentrations of the original atoms and radicals from the limiting values of the concentrations of the primary products. This last question, however, requires a separate examination.

In conclusion, the authors thank D. G. Knorre for valuable discussions.

SUMMARY

1. A method has been proposed for the experimental determination of the order in which the elementary reactions of atoms and radicals occur. The theoretical basis of the method has been given. Experimental data has been cited which exemplify the reactions of atomic oxygen and confirm the correctness of the theoretical background.

2. It has been shown that the method enables reaction products formed by a primary elementary act of an atom or radical to be distinguished from those arising by secondary and subsequent acts.

3. On the basis of the results obtained by this method, i.e. on the basis of regularities observed in the concentrations of the final products, conclusions may be drawn concerning the actual elementary reactions of atoms and radicals that are occurring.

LITERATURE CITED

[1] Problems of Kinetics and Catalysis. Collection 4, State Chem. Press, Leningrad, 1940 (see paper by A. N. Bakh, S. S. Medvedev, K. I. Ivanov, and M. B. Neiman).

[2] K. I. Ivanov, Intermediate Products and Intermediate Reactions in the Autoxidation of Hydrocarbons, State Fuel Tech. Press, 1949.

[3] W. Bone, J. Chem. Sci. 83, 1074 (1903); Proc. Roy. Soc. A129, 434 (1930); A137, 243 (1932); A143, 16 (1933); A154, 297 (1936).

[4] A. Egerton, F. Smith and A. Ubbelohde, Phil. Trans. 234, 433 (1935); A. S. Sokolik, Technology in the Air Force 4, 77 (1936).

[5] D. M. Newitt, Proc. Roy Soc. A140, 426 (1933); A147, 555 (1934); A154, 329 (1936); J. Chem. Soc. 1937, 165, 61669.

[6] R. A. Day, R. N. Pease, J. Am. Chem. Soc. 51, 1839 (1929); 57, 9296 (1935).

[7] A. R. Ubbelohde, Proc. Roy. Soc. A152, 354 (1935).

[8] M. B. Neiman, A. A. Dobrinskaya, and V. I. Gnyubkin, Mechanism of the formation of the butane cool flame, Moscow, 1940.

[9] N. N. Semenov, Prog. Chem. 20, 673 (1951).

[10] L. I. Avramenko, J. Phys. Chem. 23, 790 (1949).

[11] L. I. Avramenko and R. V. Kolesnikova, Proc. Acad. Sci. USSR 89, 1037 (1953).

[12] L. I. Avramenko and R. V. Lorentso, J. Phys. Chem. 26, 1084 (1952).

[13] L. I. Avramenko and R. V. Kolesnikova, Proc. Acad. Sci. USSR 91, 107 (1953).

Received June 18, 1954

Institute of Chemical Physics of the
USSR Academy of Sciences

BLANK
PAGE

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 3. COMPARISON OF THE RESULTS OF INVESTIGATIONS ON SODIUM BOROSILICATE GLASSES AND ON POROUS PRODUCTS OBTAINED FROM THEM BY LEACHING

E. A. Porai-Koshits, S. P. Zhdanov, and D. I. Levin

1. Relation between the Structures of the Original and the Porous Glasses

In previous communications [1, 2] we have made a survey of existing views on the causes of the opalescence of certain sodium borosilicate glasses and have described the results of experimental investigations on the Rayleigh scattering of light by the original glasses and on the structure of porous glasses prepared from them by the action of acids. In the light of these results the phenomenon of opalescence must be given a different interpretation from that advanced in the literature.

Experimental results given in the second communication have established that there is a close relationship between the structures of the original and porous glasses. It was in fact established, as a result of investigation of the structure of porous glasses by three independent methods (adsorption, low-angle scattering of X-rays, and examination under the electron microscope), that these glasses have a binary disperse structure. It was found that porous glasses have a silica skeleton having large cells or channels, the diameter of which, depending on the composition of the original glass, varies from tens to thousands of angstrom units. Within the channels there is a secondary fine structure formed from highly dispersed silicic acid, and the pores of this structure are not more than a few tens of angstrom units in diameter. The extent to which the main channels of the silica skeleton are packed with hightly dispersed silicic acid depends on the heat treatment given to the original glass and on its composition; it may vary greatly. When they are filled compactly, the intensity of the low-angle scattering of X-rays falls to an insignificant value as a result of the small difference in electron density between the channel walls and the substance filling the channels; the sorption method, however, reveals the presence of extremely fine pores having radii of the order of 10 A. When there is an almost complete absence of silicic acid in the channels, low-angle scattering gives a diffraction picture on the X-ray film in a very short time, and the large pores can be detected by the sorption method even when the porous glasses have not been treated with alkali.

When these results were considered in relation to the opalescence of the original glasses it became quite clear that opalescence is completely independent of the secondary structure, since porous glasses that are identical with respect to the dispersity of secondary silicic acid can be obtained both from strongly opalescent glasses and from completely transparent glasses. It was found also that there is an extremely close relationship between opalescence and the structure of the silica skeleton, the channels of which vary in diameter from almost 1000 A to 80-160 A, according as the original glass is opalescent or clear.

On the basis of these facts it is quite logical to suppose that the silica skeleton is present in sodium borosilicate glassss right from the beginning already before leaching. The strong scattering of light by the original glasses their opalescence is then readily explained by the differentiation of sodium borosilicate glasses, according to composition, into silica and borate components, this differentiation being the basis of the possibility of the preparation of a porous product by leaching. From this point of view, the variation in the intensity of light scattering is associated with variation in the degree of dispersion of the second component (which is dispersed within the skeleton), and hence with variation in the dimensions of the channels and walls of the silica skeleton.

The correctness of this interpretation of the phenomenon of opalescence is confirmed also by the rather high temperature at the lower limit of the opalescence zone, by the rapid increase in opalescence with further rise in temperature*, and by the dependence of the level of the higher limit of the zone on the composition of the glass. Actually, if the increase in the intensity of light scattering is associated with enlargement of the channels

---

* See Communication 1, Figures 1 and 4 [1].

of the silica skeleton, the temperature at which opalescence begins and the rate at which opalescence increases in intensity should depend on the viscosity of the glass, which falls appreciably in the temperature range of 550-700°, approximately. Comparisons of opalescence in glasses varying in composition show that the upper temperature boundary of the opalescence zone becomes lower as the amount of silica in the glass is reduced: the glass Na 75-20 (75% SiO_2) becomes clear when heated to 710-715°, whereas the glass Na 60-30(60% SiO_2) becomes clear at 685-690°*.

It must be mentioned that there is another, widely held view on the causes of opalescence. This view is in conflict with that discussed above, for it envisages a complete rearrangement of molecular bonds during leaching, and a further rearrangement during the alkali treatment of the resulting porous glass, i.e. it rejects the possibility of the existence of any sort of relationship in structure between the original glass and the porous glass, before and after alkali treatment. It is desirable, therefore, to refer to other experimental facts that confirm the existence of this relationship and show that the dimensions of the pores of the leached products can be regarded as identical with those of the regions of heterogeneity in the original glasses.

1. That the original and the porous glasses have a common structure is confirmed by the close dependence of the volume of pores and the pore dimensions on the composition of the original glass and the thermal treatment to which it has been submitted [1, 2]. Sorption and X-ray investigations have shown that in porous glasses both the total volume of pores and the pore radii increase with increase in the amount of the component of the original glasses that passes into solution (B_2O_3 and Na_2O). Also, a characteristic of porous glasses distinguishing them from silica gels is the small total volume of pores. These structural peculiarities of porous glasses indicate that, unlike silica gels, they are not completely new formations, their structures being largely predetermined by the structures of the original glasses. This conclusion is valid for all porous glasses prepared from glasses containing not less than 60% of SiO_2 (they include also glasses capable of becoming opalescent). Glasses that are poor in silica (containing less then 35% of SiO_2) yield spongy gel-like products, in no way different in structure from the usual silica gels. These products consist entirely of secondary structure, but they can no longer be regarded as porous glasses.

2. We have recently repeated an experiment originally suggested by S. E. Krasikov, and first performed by him; we modified the conditions somewhat. A fine filament of the original glass Na 70-23, diameter about 0.7 mm, was placed freely on two supports separated by a distance of 120 mm. A rod was positioned in the center of the filament so as to depress it by 5.74 mm, the depression being measured with an MIR-1 measuring microscope, suitably adapted for the purpose. In this form the filament was placed in a bath and leached with 3 N HCl for 32 hours at room temperature. When the load was removed (removal of the rod), the filament, now thoroughly treated throughout its cross section, rapidly straightened itself, so that already after the first minute the depression had diminished to 1.12 mm, after the second to 1.10 mm, after the twentieth to 0.95 mm, and so on. After 2 hours 30 minutes the depression was 0.72 mm, and after 38 hours it had reached 0.36 mm, i.e. about 6% of its maximum value, and even then slow straightening of the filament was continuing. This experiment was varied in various ways, but in all cases it was confirmed that the structure of the original glass is largely retained in the porous glass, for the leaching process did not remove internal strains produced by the applied load.

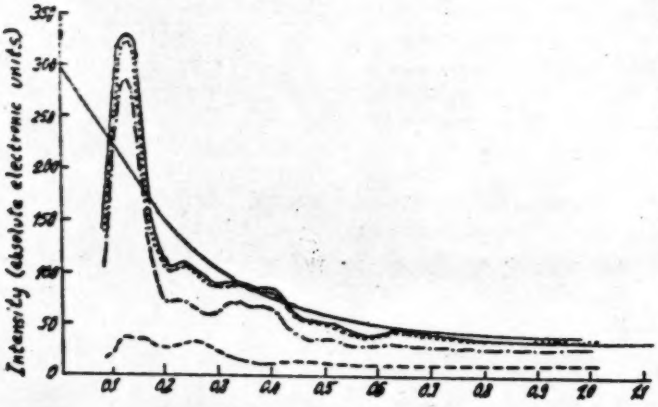


Fig. 1. Intensity curves for sodium triborate and the glass Na 70-23 (original and porous): —— Na 70-23 (experimental); —·—·—·— porous glass; . . . . . sum ($Na_2O \cdot 3B_2O_3$ + porous glass); - - - - - - - - - - - - $Na_2O \cdot 3B_2O_3$.

3. Already in 1942 one of the authors of this paper carried out an X-ray investigation of a sodium borosilicate glass that was capable of becoming opalescent [3]. In 1953 these experiments were continued under improved experimental conditions and with a large assortment of glasses (including Na 70-23 and Na 75-20) [4].

The X-ray phorographs were taken in vacuum cameras with the aid of MoK_α radiation rendered monochromatic by reflection at a calcite monocrystal. The phorographs were exam-

* See Communication 2, Fig. 10 [2].

ined with a recording microphotometer and intensity curves were determined, the intensity being expressed in absolute electronic units (polarization, absorption, and incongruent scattering were taken into account). It was again confirmed that the intensity curve of the original glass can be represented as the sum of the curves for vitreous sodium borate and for the porous glass obtained by treating the original glass with hydrochloric acid (Fig. 1). This provides direct proof that silica skeleton, regarded not only submicroscopically, but also at the atomic level, is already present in the original sodium borosilicate glasses and is not formed in the course of chemical reaction between the sodium silicates of borates of the original glass and the acids with which it is treated. The absence of even a small discrepancy between the summative and experimental curves for the original glasses in the region of the main intensity maximum indicates how negligible is the effect of the boundary layer or of the intermediate layer, heterogeneous in composition, between regions differing in chemical composition and large in size in comparison with the transitional layer.

4. The common structure of the original and porous glasses is confirmed also by the striking symbatic relationship between the curves (which have obvious anomalies) for the dependence of many physical and chemical properties of the original glasses (density, refractive index, chemical stability, etc.) on temperature and the curves characterizing the structure of porous glasses prepared from the original glasses at the corresponding temperatures [5].

The dimensions of the regions consisting of dispersed component – evaluated from measurements of the diameters of the main channels of the porous products obtained by leaching – are 600-1000 A for opalescent glasses; they can be regarded as small in comparison with the wavelength of visible light, and light scattered by such regions should be mainly polarized, which is in accord with depolarization measurements in the opalescence zone [6].

When the temperature is raised above a value that is characteristic for each composition, the opalescence disappears as a result of a great reduction in the dimensions of the channels of the silica skeleton and a corresponding increase in the degree of dispersion of the second component, which has an extremely low viscosity at this temperature. The disappearance of opalescence is a phenomenon similar to that observed in liquid mixtures near to the temperature of complete solution. However, the glass does not become completely homogeneous, and at temperatures 50-100° above that at which opalescence disappears it continues to retain the two independent structures, the degree of dispersion, however, being much higher than it is in opalescent glasses. The dimensions of the regions of heterogeneity are now 80-150 A, again estimated from measurements of the diameters of the channels in porous glasses, and the distribution of the regions according to size is much narrower in clear glasses than in opalescent glasses.

With regard to the chemical composition of the component dispersed within the silica skeleton, the suggestion of Grebenshchikov [7] that sodium oxide undergoes redistribution between B_2O_3 and SiO_2 as the temperature changes – which he based on the analysis of the dry residue from the acid extract – has been confirmed in the present work. The formation of various compounds between Na_2O, B_2O_3, and SiO_2 within this component of the original glass will, in fact, result in a variation in the compactness with which the channels of the porous glass are filled with secondary silicic acid – and this is what is actually observed. Accepting Grebenshchikov's suggestions, we may describe the variation of the composition of the dispersed component with temperature as follows.

At low temperatures, when the change in the intensity of Rayleigh scattering is reversible and the main channels of the porous glass obtained by leaching are filled with not very closely packed secondary silicic acid, it is probable that reversible chemical reactions of some sort occur in the glass with the participation of all of the three oxides Na_2O, B_2O_3, and SiO_2. At the temperature of minimum scattering, which is characterized also by almost complete absence of secondary silicic acid in the main channels of the porous glass obtained by leaching, it must be assumed the $Na-O-B\diagup\diagdown$ linkages are formed preferentially, rather than $Na-O-\underset{|}{\overset{|}{Si}}-$ linkages, which should facilitate dissolution of the dispersed component in the skeleton and the formation of clean channels. Finally, at temperatures in the opalescence zone, which is characterized not only by maximum scattering intensity, but also by the formation of a porous glass having channels that have an extremely compact filling of secondary silicic acid, it is most probable that sodium silicates take an active part in chemical leaching reactions, and these silicates, being hydrolyzed in the course of the leaching, are a source of silicic acid gel, which forms a compact filling in the channels (secondary structure).

When the temperature is raised above 550°, there is a rapid increase in the dimensions of the regions of heterogeneity which is accompanied by the appearance of opalescence, and this process, as pointed out in our first communication, is irreversible: if we begin to lower the temperature from some value in the opalescence zone, then a part of the curve from 530° to 20° can be reproduced (with a characteristic minimum at 530°), only at a high value of absolute intensity (curve a', b', c', Fig. 2). The reversibility of relative changes in this temperature region must be associated with the same processes of chemical redistribution, but they now occur in large regions of heterogeneity. Only when we pass beyond the temperature at which opalescence disappears do these large regions break down again into small ones, so that the whole process can be repeated once more.

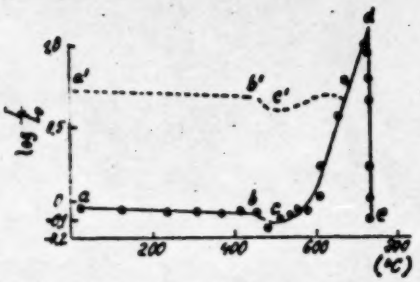


Fig. 2. Dependence of the intensity of light scattering on temperature for the glass Na 70-23

2. Microheterogeneous Structure of Complex Glasses

The facts discussed in the first section, and also the experimental results given in previous communications, confirm the general views of Grebenshchikov on the peculiar "submicroheterogeneity" of complex glasses, and they permit us to describe the structure of the sodium borosilicate glasses that we have studied in the following manner.

Sodium borosilicate glasses that are capable of showing opalescence have a silica skeleton, and the cells of this skeleton are filled with a second component containing boron, sodium, and silicon oxides, which, according to the composition and temperature, form various chemical compounds. These regions of qualitative heterogeneity provide the source of the scattering of light in varying degree right up to strong opalescence. The peculiar "microheterogeneity" or "two-phase character" (the term " phase" is not, of course, to be understood in the sense of the classical definition) of sodium borosilicate glasses is not exceptional among complex glasses. It would be more true to say that these glasses form a more suitable object for investigation in the study of the general laws governing the structure of complex glasses, since they enable an approach to be made by a combination of different methods of X-ray structural analysis (scattering at high and at low angles) with other physicochemical methods. Similar properties are possessed by other alkali borosilicate glasses, such as potassium and lithium, and probably also by some phosphate and aluminosilicate glasses, etc.

In a recently published paper [8] describing an electron-microscope investigation of the vitreous silica in two commercial glasses of fairly complex composition, a lead glass, and some sodium borosilicate glasses having Na_2O contents of 16-30 mole-%, photographs are given that reveal the presence of a grain structure in all of the glasses, and the dimensions of the grains, depending on the composition and the thermal treatment of the glass, vary from 15-20 to 200 A. In some of the glasses the regions of heterogeneity are extremely regular in form. When the glass is drawn into filaments, the grains are drawn out into chains, which are oriented along the axis of the filament. A photograph of the silica skeleton obtained at the surface of one of the glasses as a result of its treatment with acid is of great interest. The authors consider that the glasses have heterogeneous structures and contain micellar regions that are higher in electron density and more regular in structure than the surrounding medium.

In a recently published paper, Indenbom [9] states that two different strain-relaxation zones occur in the glasses that he has investigated (their compositions are not given in the paper), these zones being associated with the occurrence of strains of the second kind that are compensated in micro-spaces. These strains result in anomalous birefringence, which does not disappear in the usual annealing process. The author associates these phenomena with the presence of two phases differing in softening temperature, i.e. with a microheterogeneous structure. The results of Debye and Bueche [10] on the intensity of light scattered at various angles from two optical glasses are to be interpreted in the same way. Using the theory proposed by Debye, the authors calculated the dimensions of the regions of heterogeneity from the scattering indicatrices; for the radii of the regions they found 296 A for borosilicate glass and 269 A for heavy flint glass. If we take the difference in the compositions of the glasses into account, these results are in close accord with the results of the investigation described in our second communication [2].

Already in 1943 [11] one of the authors of the present paper showed by X-ray investigation that certain binary glasses (sodium silicate, borosilicate, and sodium borate glasses) have "microheterogeneous" structures. Supplementary experiments carried out recently [4] have shown that for sodium silicate glasses a small amount of additional scattering of X-rays can be detected (not accounted for by the scattering of the components). This results from the presence of an intermediate "chemically disorganized" part of the glass, which binds the vitreous silica and sodium metasilicate together. This result indicates that the chemically homogeneous regions cannot be as large as those in sodium borosilicate glasses that are capable of becoming opalescent. The additional scattering found at relatively low angles ($\frac{\sin\theta}{\lambda} \approx 0.15$), must be associated with the effect of matter distributed at the surface of each chemically homogeneous region or "phase", and the significance of such a boundary effect will grow as the size of such a region is reduced. It may be mentioned that a similar result was recently obtained by Danilov [12], who made an X-ray investigation of acetone-water solutions; on the scattering curves the first principal maximum was not resolved, whereas it was resolved on the curve obtained by simple summation.

In this connection we may mention investigations on two-component sodium and potassium silicate glasses

carried out by the Raman spectrum method at the Institute of Silicate Chemistry by Kolesova [13]. These results confirmed that, in these glasses, regions of heterogeneity of the order of 100 A and more in diameter, such as are present in sodium borosilicate glasses, are absent. Variations with composition of the frequencies and intensities of certain bands in the spectrum are to be expected if the regions of chemical heterogeneity are small enough for atoms in one region to effect the vibrations of atoms in another, which is in accord with the presence of the "boundary effect" that we detected by X-rays. Similar results are obtained for borosilicate glasses: porous glasses prepared from these were investigated by one of the present authors by sorption methods, and it was found possible to estimate the radii of the pores, which were found to be about 10 A. These results were confirmed in an investigation of the same glasses by the method of low-angle scattering of X-rays.

All these facts, and all the variety of experimental material obtained in the study of many complex glasses by various methods of physicochemical analysis [7, 14-23], have convinced us of the fruitfulness of theconcept of the microheterogeneous structure of complex glasses–of the existence in them of "chemical order"– a concept that has caused many foreign investigators of the hypothesis of a disordered lattice to publish papers in recent years in which they acknowledge the need for a re-examination of the basis of this hypothesis [24-28].

The prolonged polemics between supporters of the disordered-lattice hypothesis and those of the crystallite hypothesis on the question of the degree of "physical order" in the disposition of the atoms has ended in the general development of the compromise view, according to which there are points of maximum order, which can be logically termed crystallites, in the continuous disordered lattice. Such crystallites, however, cannot be more than 10-20 A in size and have nothing in common with the regions of heterogeneity, which may be much larger. These regions themselves have continuous lattices with crystallites at particular points, and they differ among themselves in chemical composition. The development of the hypothesis of the microheterogeneous structure of complex glasses and the interpretation on its basis of the physicochemical properties of glasses – and not the continuation of the groundless dispute about the crystallite and disorder theories of structure – these form the immediate problem of the investigators of the vitreous state.

SUMMARY

1. It has been established that sodium borosilicate glasses that are capable of becoming opalescent and the porous glasses obtained from them by leaching have a common structure.

2. The light scattering and opalescence of sodium borosilicate glasses result from their differentiation into silica and borate components, and it is this differentiation that makes it possible to obtain porous products by leaching.

3. The variation in the intensity of the scattering of light by sodium borosilicate glasses is associated with the variation in the degree of dispersion of the second component, i.e. the borate component that is dispersed through the skeleton.

4. The dimensions of the chemically homogeneous regions in sodium borosilicate glasses have been estimated by a study of the structure of the corresponding porous glasses.

5. The presence of local chemical order (submicroheterogeneous structure) is characteristic not only for sodium borosilicate glasses, but also for most complex glasses.

LITERATURE CITED

[1] D. L. Levin, S. P. Zhdanov, and E. A. Porai-Koshits, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 31. •

[2] S. P. Zhdanov, E. A. Porai-Koshits, and D. L. Levin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 197. ••

[3] E. A. Porai-Koshits, Proc. Acad. Sci. USSR 36, 285 (1942); J. Gen. Chem. 12, 196 (1942).

[4] E. A. Porai-Koshits, Doctorate thesis, Leningrad, 1953.

[5] S. P. Zhdanov, Thesis, Leningrad, 1950.

[6] D. L. Levin, Thesis, Leningrad, 1951.

• Consultant's Bureau Translation, p. 27.

•• Consultant's Bureau Translation, p. 177.

[7] I. V. Grebenshchikov and O. S. Molchanova, J. Gen. Chem. 12, 588 (1942).

[8] A. F. Prebus, J. W. Michener, Ind. Eng. Chem. 46, 147 (1954).

[9] V. L. Indenbom, Proc. Acad. Sci. USSR 89, 509 (1953).

[10] P. Debye, A. M. Bueche, J. Appl. Phys. 20, 518 (1949).

[11] E. A. Porai-Koshits, Proc. Acad. Sci. USSR 40, 394 (1943).

[12] V. I. Danilov, A. M. Zubko, and A. I. Danilova, J. Expt. Theor. Physics 19, 242 (1949).

[13] V. A. Kolesnikova, Thesis, Leningrad, 1953.

[14] K. S. Evstropyev, Bull. Acad. Sci. USSR, Physics Series 4, 616 (1940).

[15] K. G. Kumanin, Bull. Acad. Sci. USSR, Physics Series 4, 588, (1940).

[16] O. K. Botvinkin, Bull. Acad. Sci. USSR, Physics Series 4, 600 (1940).

[17] R. Müller, C. Weinstein, Acta. Phys. Chim. USSR, 3, 465 (1935).

[18] R. Müller, P. Markin, Acta. Phys. Chim. USSR, 4, 471 (1936).

[19] R. Müller, Acta. Phys. Chim. USSR, 1, 407 (1932); 4, 99 (1936); 4, 481 (1936).

[20] R. Myuller, Bull. Acad. Sci. USSR, Physics Series 4, 607 (1940).

[21] A. M. Venderovich, V. A. Presnov, and V. I. Chernykh, Collection in Honor of the 70th Birthday of Academician A. F. Ioffe, 192, 1950.

[22] B. I. Markin, J. Theor. Physics 22, 932 and 941 (1952).

[23] O. A. Esin, Bull. Acad. Sci. USSR, Chem. Series No. 6, 561 (1948).

[24] W. A. Weyl, J. Soc. Glass Techn. 35, 421, 448, 462, 469 (1951).

[25] W. A. Weyl, Phase Transformations in Solids, New York and London, 1951.

[26] A. G. Smekal, J. Soc. Glass Techn. 35, 411 (1951).

[27] N. J. Kreide, Glass. Ind. 31, 573 (1950).

[28] J. M. Stevels, Philips Tech. Rund. 13, 350 (1952).

Received April 2, 1954

Institute of Silicate Chemistry of
the USSR Academy of Sciences

REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 6. REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH CAUSTIC ALKALI SOLUTIONS

S. K. Dubrovo and Yu. A. Schmidt

We have previously studied the action of water and acid solutions on vitreous sodium silicates and aluminosilicates [1-4]. In alkaline solutions the mecahnism of the breakdown of these glasses is different from that in acid solutions, and such comparison that can be made with the behavior in water is to be attributed to the fact that in such a treatment an alkaline solution is formed. In treatments with water, and particularly with solutions of acids, protective silicic or aluminosilicic acid films formed on the surface of the glass play an essential part in the breakdown process by controlling the rate of ion exchange between the glass that is as yet unchanged and the solution. When sodium silicates are treated with caustic alkali solutions, either no film at all is formed, or the film formed is a porous one.

When there is no film, the rate at which the glass is broken down is no longer determined by ionic diffusion through a film, but is determined directly by the exchange of ions from the surface of the glass with ions from the solution. The rate at which the silica of the glass reacts with alkali is also to be associated with this process.

There are very few data in the literature on the interaction of vitreous sodium silicates and aluminosilicates with alkaline solutions. The work of Dimbleby and Turner [5] is noteworthy: these authors investigated the action of 2N solutions of sodium carbonate and caustic soda on sodium silicates ($Na_2O \cdot 2SiO_2$, $Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 4SiO_2$) and also on aluminosilicates in which Na_2O was replaced by Al_2O_3 (over the range 0.12-0.30 of a molecular proportion) in the silicate $Na_2O \cdot 3SiO_2$. As the Na_2O content of the sodium silicates fell, their stability toward sodium carbonate solution increased greatly, whereas, their stability towards caustic soda solution changed only slightly; the first of these solutions had much the stronger disrupting action. As Na_2O was replaced in the silicate by Al_2O_3, the first portions of the aluminum oxide were more effective, succeeding portions having little effect on the stability of the glasses. From their experiments, the authors do not make any inferences relating to the mechanism of the breakdown of the glasses by alkaline solutions.

In the present investigation we have studied the character of the interaction of vitreous sodium silicates and aluminosilicates with solutions of caustic alkali. With this object we have investigatedthe breakdown produced by caustic alkali solutions of various concentrations in sodium silicates of composition in the range $Na_2O \cdot 1.4SiO_2$ to $Na_2O \cdot 6SiO_2$, and also in quartz glass and in sodium aluminosilicates consisting of sodium disilicate with additions of 0.05-1 molecular proportion of aluminum oxide. As in previous investigations, the breakdown of the glasses was characterized by the amount in moles of the oxides that passed into solution from 1 sq. cm of glass surface (n_{Na_2O}, n_{SiO_2} and $n_{Al_2O_3}$).

EXPERIMENTAL

Reaction of Vitreous Sodium Silicates with Caustic Alkali Solutions. In order to determine the dependence of the tendency for sodium silicates to undergo breakdown on their silica contents and on the pH of the solution, experiments were carried out on eight sodium silicates treated in caustic soda solutions varying in concentration from 0.01 to 3 N. Also, the stabilities of powdered quartz glass and sodium disilicate after acid treatment were determined. After the leaching treatment, the disilicate contained 81.2% SiO_2, 0.54% Na_2O, and 18.3% H_2O [6]. In view of the fact that the properties of the acid-treated sodium silicate powder should be similar in properties to the siliceous film formed on the surface of this silicate, a study of the rate of solution of this powder was of some interest. The test specimens of sodium silicate were in the form of disks, 10-12 sq. cm in area. The powders of quartz glass and treated sodium disilicate had a grain size of 140-200μ. The results of the tests on these were also related to 1 sq. cm of surface, this being effected by calculation. The experiments were carried out at 40° in a silver apparatus.

TABLE 1

Reaction of Vitreous Sodium Disilicate with Caustic Soda Solutions

Solution	Index	Time (hours)					
		0.5	1	2	4	6	8
Water	$n_{Na_2O}(\times 10^{-6})$	11	18	30	47	62	76
	$n_{SiO_2}(\times 10^{-6})$	2.3	3.2	4.2	5.8	9.3	13
	α	0.10	0.09	0.07	0.06	0.08	0.09
0.01 N NaOH	$n_{Na_2O}(\times 10^{-6})$	7.0	11	21	40	59	–
	$n_{SiO_2}(\times 10^{-6})$	2.7	4.7	11	39	72	–
	α	0.19	0.21	0.26	0.49	0.60	–
0.01 N KOH	$n_{Na_2O}(\times 10^{-6})$	–	4.9	12	28	50	64
	$n_{SiO_2}(\times 10^{-6})$	–	2.7	7.9	39	72	109
	α	–	0.24	0.32	0.70	0.72	0.84
0.1 N NaOH	$n_{Na_2O}(\times 10^{-6})$	3.2	4.8	7.7	15	24	–
	$n_{SiO_2}(\times 10^{-6})$	4.6	7.9	15	31	49	–
	α	0.72	0.82	0.97	1.0	1.0	–
1.0 N NaOH	$n_{Na_2O}(\times 10^{-6})$	0.09	0.17	0.33	0.5	0.70	–
	$n_{SiO_2}(\times 10^{-6})$	0.18	0.35	0.67	1.1	1.4	–
	α						

The amount of SiO_2 passing into solution was determined, as before, by a colorimetric method. The amount of Na_2O passing into solution [illegible] in the experiments with 0.01-0.1 N solutions of caustic soda was determined from the change in the titer of the solution, change in concentration due to evaporation being taken into account. For N NaOH the determination of Na_2O was not carried out, and the values of n_{Na_2O} given in the table were calculated from n_{SiO_2}, since, on the basis of the 0.1 N NaOH experiments, it could be assumed that in this experiment dissolution of the glass occurred. In experiments with caustic potash solution, Na_2O was determined colorimetrically. The results are given in Tables 1 and 2, and also in Figures 1 and 2. For comparison, results obtained previously [1] for the reaction of the same sodium silicates with water are also given.

Table 1, which relates to the reaction of vitreous sodium disilicate with caustic alkali solution for various times, shows that the amount of Na_2O passing into solution diminishes as the concentration of alkali increases. In weakly alkaline solution (up to 0.1 N), the passage of SiO_2 into solution lags behind that of Na_2O, so that a siliceous film remains on the surface of the sodium disilicate (α i.e. the fraction of the SiO_2 originally present in the reacting layer of glass which has passed into solution is less than unity).

Dissolution of the residual siliceous film greatly increases as we pass from water to 0.01 N NaOH. In experiments with 0.1 N NaOH the value of n_{SiO_2} is increased in comparison with the value in weaker solutions only while a siliceous film remains on the surface. When, however, the film has disappeared as a result of complete dissolution, the amounts of SiO_2 going into solution are less than in the 0.01 N NaOH experiments. This is even more marked when we pass to N NaOH, when dissolution of the glass appears to occur right from the start of the treatment. The rate at which SiO_2 passes from the sodium disilicate into solution is then much less in comparison with the behavior in less concentrated solutions. In a treatment with 0.01 N KOH, the rate of breakdown of the sodium disilicate is less at the beginning of the experiment than it is in the caustic soda solution of the same concentration. In the course of time, however, this difference disappears. With respect to the rate at which Na_2O passes into solution, breakdown of the siliceous film is appreciably more rapid in the caustic potash solution, a fact that can be deduced from a comparison of the values of α.

The data in Table 2 characterize the breakdown of sodium silicates and quartz glass by caustic soda solutions. In the case of the silicate $Na_2O \cdot 1.4SiO_2$, simple treatment with water results almost in the dissolution of the glass, and no siliceous film is formed on the surface. As the concentration of alkali increases, the amount of SiO_2 passing into solution falls rapidly. For the silicate $Na_2O \cdot 1.7\ SiO_2$, transition to dissolution occurs only when the caustic soda solution is increased to 0.01 N, and there is an associated increase in n_{SiO_2} in comparison with water. With further

increase in the alkali concentration, the value of n_{SiO_2} again begins to fall. As we saw above, a similar picture is observed for sodium disilicate. With increase in the silica content of the sodium silicate, n_{SiO_2} falls as can be seen from Fig. 1. The relation of the amount of SiO_2 passing into solution to the silica content is expressed by a smooth curve, as can beseen in the experiments with 0.1 N NaOH, taken as an example (Fig. 1).

TABLE 2

Tendency for Vitreous Sodium Silicate and Quartz Glass to undergo Breakdown in Caustic Soda Solutions (Duration of treatment 1 hour)

Concentration of solution	Index	Molar ratio $Na_2O : SiO_2$								Quartz glass
		1:1.4	1:1.7	1:2	1:2*	1:2.3	1:2.6	1:3	1:6	
Water	n_{Na_2O} ($\times 10^{-5}$)	439	51	18	–	9.1	–	1.6	0.30	–
	n_{SiO_2} ($\times 10^{-5}$)	605	33	3.2	0.15	0.24	–	0.04	0.009	–
0.001 N NaOH	n_{SiO_2} ($\times 10^{-5}$)	–	–	–	0.85	–	–	–	–	0.003
0.01 N NaOH	n_{Na_2O} ($\times 10^{-5}$)	–	56	11	–	–	–	–	–	–
	n_{SiO_2} ($\times 10^{-5}$)	–	99	4.7	5.8	–	–	–	–	0.009
0.1 N NaOH	n_{Na_2O} ($\times 10^{-5}$)	–	–	4.8	–	–	–	–	–	–
	n_{SiO_2} ($\times 10^{-5}$)	210	36	7.9	9.2	1.25	0.17	0.12	0.16	0.024
1.0 N NaOH	n_{SiO_2} ($\times 10^{-5}$)	14	1.3	0.35	24	–	–	0.06	–	0.055
3.0 N NaOH	n_{SiO_2} ($\times 10^{-5}$)	–	–	–	–	–	–	0.04	–	0.083

* treated powder.

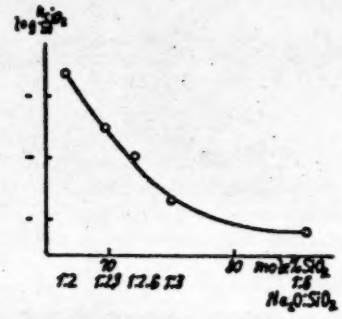


Fig. 1. Dependence on the composition of the glass of the amount of silicic acid passing into solution during a 6-hour treatment of vitreous sodium silicates with 0.1 NaOH (the values of n_{SiO_2} are based on the SiO_2 content of the glass when its composition is expressed in the form $Na_2O \cdot mSiO_2$).

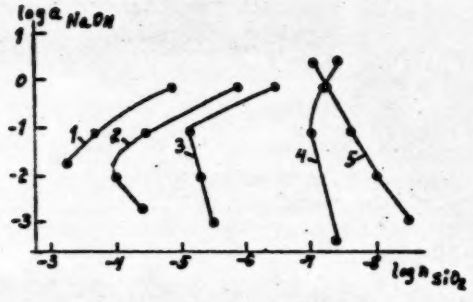


Fig. 2. Dependence on the activity of NaOH of the amount of silicic acid passing into solution during a one-hour treatment of vitreous sodium silicates and quartz glass with caustic soda solutions: 1-$Na_2O \cdot 1.4SiO_2$; 2- $Na_2O \cdot 1.7SiO_2$; 3- $NaO_2 \cdot 2SiO_2$; 4- $Na_2O \cdot 3SiO_2$; 5- quartz glass.

The rate of solution for powders of treated sodium disilicate and quartz glass increases continuously as the alkali concentration increases. The value of n_{SiO_2} for the first is 300-600 times as great as that for the second.

Reaction of Vitreous Sodium Aluminosilicates with Solutions of Caustic Alkalis. A study was made of the action of 0.1 N NaOH on six aluminosilicates prepared by the addition of aluminum oxide to sodium disilicate. We estimated the extent and character of the breakdown by the amounts of Al_2O_3 and SiO_2 that passed into solution (which were determined colorimetrically) and by the ratio of the amounts in the solution expressed as $\gamma = n_{SiO_2} / n_{Al_2O_3}$. The results are given in Table 3.

It will be seen from these results that the first additions of aluminum oxide to sodium disilicate greatly reduce the amounts of SiO_2 passing into solution. When the alumina content of the investigated aluminosilicates is increased

TABLE 3

Reaction of Sodium Aluminosilicates with 0.1 N Caustic Soda at 40°

Molar proportions $Na_2O : Al_2O_3 : SiO_2$	Ratio $\frac{SiO_2}{Al_2O_3}$ in original glass	Index	Time (hours) 1	2	4	6	8
1 : 2	–	$n_{SiO_2}(\times 10^{-6})$	7.9	15	31	49	53
1 : 0.05 : 2	40	$n_{SiO_2}(\times 10^{-6})$	0.18	0.75	1.47	2.24	3.10
		$n_{Al_2O_3}(\times 10^{-6})$	0.01	0.02	0.04	0.054	0.075
		γ	18	38	37	41	41
1 : 0.15 : 2	13.3	$n_{SiO_2}(\times 10^{-6})$	–	0.42	0.57	0.76	0.93
		$n_{Al_2O_3}(\times 10^{-6})$	0.01	0.01	0.02	0.03	0.035
		γ	–	42	28	25	27
1 : 0.25 : 2	8	$n_{SiO_2}(\times 10^{-6})$	0.17	0.26	0.40	0.51	0.52
		$n_{Al_2O_3}(\times 10^{-6})$	0.014	0.023	0.032	0.038	0.053
		γ	12.1	11.3	12.5	13.4	9.8
1 : 0.40 : 2	5	$n_{SiO_2}(\times 10^{-6})$	0.08	0.11	0.18	0.22	0.25
		$n_{Al_2O_3}(\times 10^{-6})$	0.01	0.02	0.025	0.037	0.047
		γ	8	5.5	7.2	6.0	5.3
1 : 0.50 : 2	4	$n_{SiO_2}(\times 10^{-6})$	0.19	0.26	0.30	0.43	0.45
		$n_{Al_2O_3}(\times 10^{-6})$	0.019	0.02	0.04	0.05	0.074
		γ	10	13	7.5	8.6	6.1
1 : 1 : 2•	2	$n_{SiO_2}(\times 10^{-6})$	–	–	0.35	0.43	0.51
		$n_{Al_2O_3}(\times 10^{-6})$	–	–	0.093	0.13	0.16
		γ	–	–	3.7	3.3	3.2

further up to 0.4 of a molecular proportion, although n_{SiO_2} again falls the additions are now less effective, and when the addition exceeds 0.4 of a molecular proportion, n_{SiO_2} begins to rise somewhat, indicating an intensification of the attack on the aluminosilicates. The values of $n_{Al_2O_3}$ vary in an analogous way, when related to the alumina content of the original glass. The values of γ given in Table 3 show that the ratio $\frac{SiO_2}{Al_2O_3}$ for the solution is not the same as for the original glass. For all of the aluminosilicates investigated, with the exception of that containing 0.05 of a molecular proportion of Al_2O_3, this ratio is higher for the solution than for the glass. Consequently, the surface of the aluminosilicates becomes enriched in aluminum ions. We have previously observed a similar phenomenon for the reaction of sodium aluminosilicates with water [3]. It is possible that the enrichment of the surface in aluminum ions is the result of a secondary process – adsorption of aluminum ions passing into solution by the residual alumina-silica layer.

DISCUSSION OF RESULTS

In our previous investigations [6] we have concluded that, when a siliceous film is present on the surface of a vitreous sodium silicate, increase in the alkali content of the solution (i.e. increase in the concentration of sodium ions and reduction in the concentration of hydrogen ions) should result in an increase in the concentration of sodium ions in the film at its boundary with the solution. As a result, the sodium ion concentration gradient in the film is reduced, and therefore also the rate of diffusion of sodium ions through the film into the solution. As the alkali concentration increases (in the sodium disilicate experiments, up to about 0.1 N), a point is reached

• In the glass 1 : 1 : 2 there were small regions containing crystalline occlusions.

at which complete dissolution of the siliceous film on the glass surface will occur. The rate at which sodium ions pass into solution will then be determined directly by the ion-exchange process at the glass surface. It is here necessary to remember that the experimentally observed rate of passage of sodium ions from the glass into solution (v_{Na^+}) is essentially the difference between the actual rates of transfer in the two directions:

$$v_{Na^+} = v_{Na^+}' - v_{Na^+}'' = v_{H^+}$$

(v_{Na} is the rate at which sodium ions pass from glass to solution, v_{Na^+}'' is the rate at which they pass in the opposite direction, and v_H is the rate at which hydrogen ions pass into the glass.). Since the sodium ion concentration is high in strongly alkaline solutions and the hydrogen ion concentration is very low, in such solutions the rate at which sodium ions pass from solution to glass (v_{Na^+}') will probably differ only slightly from the rate of their passage into solution (v_{Na^+}''). The probability of the passage of hydrogen ions into the glass, which is proportional to their concentration, is very low, so that the velocities v_{Na^+} and v_{H^+} are also low. Increase in the concentration of alkali results in a considerable reduction in the rate at which hydrogen ions pass into the galss, and therefore also in v_{Na^+}.

As will be seen from the results of the experiments, when the alkali concentration is increased, the rate at which silica passes from sodium silicates into solution increases only while there is a residual siliceous film on the surface. When, however, this film has dissolved, the rate at which silica passes into solution falls as the alkali concentration rises. If, under these circumstances, dissolution of the silica of the glass were an independent process, increase in the alkali concentration would result in a continuous increase in the rate at which SiO_2 passes into solution, and therefore also in the rate at which Na_2O passes into solution. The behavior observed is in fact the reverse of this. It may therefore be assumed that, in the interaction of vitreous sodium silicates with strongly alkaline solutions, the rate at which the silica of the glass is dissolved depends on the rate of the primary process of exchange of sodium ions for hydrogen ions from the solution. The entry of hydrogen ions (probably more exactly, H_3O^+) probably facilitates the addition of water at one of the Si — O — Si linkages of a neighboring silicon-oxygen tetrahedron and, under alkaline conditions, this is a stimulus to the complete breakaway of this tetrahedron from the glass surface. It is probable that such a breakaway occurs immediately after the addition of a hydrogen ion to the SiO_4 tetrahedron, so that there is always a fresh glass surface in reaction with the solution, and it is almost completely saturated with sodium ions. The hydrogen ion concentration in the surface layer is however so low that there is no surface film.

The difference between the treated powder and the fresh surface lies in the fact that in the former the sodium ions have already been replaced by hydrogen ions. In this way conditions have already been set for the subsequent dissolution of the powder in an alkaline medium, so that with increase in alkali concentration the rate of dissolution increases continuously.

The reduction in the rate of dissolution with increase in the alkali content of the solution is particularly notable for sodium disilicate and for more alkaline silicate, i.e. for glasses in which each SiO_4 tetrahedron is associated, on the average, with not less than one sodium ion. In the case of the silicate $Na_2O \cdot 3SiO_2$, however, we may suppose that silicon-oxygen tetrahedra are present which are not associated with sodium ions, and the maximum on the curve for the dependence of the rate at which SiO_2 passes into solution on the alkali concentration is much more poorly defined. The rate at which quartz glass dissolves increases continuously with increase in alkali concentration. It may therefore be supposed that the rates of dissolution of silicon-oxygen tetrahedra associated in the glass with sodium ions and of those united only with other SiO_4 tetrahedra depend in different ways on the alkali concentration. The breakaway of tetrahedra of the first kind from the surface will probably occur, under the given conditions, soon after the passage of the associated sodium ions into solution, so that with increase in alkali concentration and reduction in v_{Na^+} there will be a reduction in the rate at which the tetrahedra pass into solution. On the other hand, the rate of dissolution of the SiO_4 tetrahedra that are not associated with sodium ions will rise continuously with increase in alkali concentration, as can be seen from the behavior of quartz glass. The mechanism of this process is not yet altogether clear, but it is probable that in this case also an essential part is played by the presence on the surface of quartz glass of Si — OH groups capable of taking part in ion exchange.

It is of interest also to compare the rates at which quartz glass and acid-treated sodium disilicate powder dissolve in alkalis. Since the degree of polymerization of silica in sodium disilicate is lower than in quartz glass, its silicon-oxygen skeleton will undergo appreciable hydration when treated with acid. It is to be expected that the reactivity of such a powder will be considerably higher than that of quartz glass, and this is confirmed by comparison of the values of n_{SiO_2}.

In the light of these considerations it is possible to explain also the results of the experiments of Dimbleby and Turner [5] mentioned above on the determination of the stabilities of sodium silicates in caustic soda and sodium

carbonate solutions. The higher rate at which these silicates are broken down in the sodium carbonate solution is probably to be associated with the fact that in this solution the hydrogen ion activity is higher and the sodium ion activity lower than in the caustic soda solution.

As can be seen from the data in Table 2 and Fig. 1, with increase in the silica content of the silicates, the rate at which they are broken down in alkali solutions falls. This indicates that in the present case the degree of polymerization of silica in the silicon-oxygen skeleton of the glass is one of the main factors determining the rate of breakdown.

In comparing the destructive effects of caustic soda and caustic potash solutions on sodium disilicate, we have found that in the course of time the difference in the rate at which sodium ions pass from the glass to the solution disappears. This phenomenon is probably associated with the presence on the surface of the sodium disilicate of a siliceous film that controls the rates at which sodium and potassium ions diffuse. As can be seen from the data in Table 1, in the course of time the siliceous film is largely broken down (α increases), and the process of ionic diffusion through the film gradually loses its determining role.

An examination of the results obtained on the tendency for the investigated aluminosilicates to be broken down in caustic alkali solutions shows that small additions of aluminum oxide to sodium disilicate have a greater effect in improving alkali-stability than the equivalent additions of silica. For example, the stability of the aluminosilicate $Na_2O \cdot 0.15Al_2O_3 \cdot 2SiO_2$ to an eight-hour treatment in 0.1 N NaOH was found to be ten times as high as that of the corresponding silicate $Na_2O \cdot 2.3SiO_2$ (see Tables 2 and 3). With further increase in the alumina content, the rate of the dissolution of the aluminosilicates is now reduced to a lesser extent, and, beginning from the composition $Na_2O \cdot 0.5Al_2O_3 \cdot 2SiO_2$, it even rises somewhat. Here we see the influence of the previously noted effect of the depolymerization of the silicon-oxygen part of the glass skeleton as the aluminum oxide content increases. Thus, in the examination of the alkali-stability of vitreous sodium aluminosilicates it is again necessary to take into consideration the degree of polymerization of silica in the original glass.

SUMMARY

1. A study has been made of the interaction with caustic alkali solutions of sodium silicates in the range $Na_2O \cdot 1.4SiO_2$ - $Na_2O \cdot 6SiO_2$, of vitreous silica, and of sodium aluminosilicates consisting of sodium disilicate with an addition of 0.05-1 molecular proportion of aluminum oxide.

2. With increase in alkali concentration, the rate at which sodium ions pass into solution from the investigated silicates diminishes. The rate at which SiO_2 passes into solution increases while a residual siliceous film still remains on the surface. However, after the dissolution of this film, the rate at which the silica of the glass passes into solution diminishes as the alkali concentration increases.

3. As the silica content of silicate glasses increases, their tendency to undergo breakdown in solutions of caustic alkalis is reduced.

4. Small additions of alumina to vitreous sodium disilicate are more effective in increasing alkali-stability than equivalent additions of silica. When, however, the molecular proportion of alumina is increased to 0.5 or more, the rate of breakdown of the aluminosilicate increases somewhat, probably owing to depolymerization of the silicon-oxygen part of the skeleton.

LITERATURE CITED

[1] S. K. Dubrovo and Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 4, 597 (T.p.535*).

[2] S. K. Dubrovo, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 244.** (T.p. 197)*.

[3] Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 778.

[4] S. K. Dubrovo, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 770.

[5] V. Dimbleby, W. E. S. Turner, J. Soc. Tech., 10, 304 (1926).

[6] Yu. A. Schmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 236.(T.p.191)*.

Received June 30, 1954

Institute of Silicate Chemistry of the
USSR Academy of Sciences

* T.p. = Consultant's Bureau Translation pagination.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 9. THE TERNARY SYSTEM LiOH – H_2O_2 – H_2O

S. Z. Makarov and T. A. Dobrynina

Unlike the peroxide compounds of sodium, potassium, rubidium, and cesium, of which the literature reports a number of the types M_2O_2 and M_2O_4 or MO_2 together with perhydrate and hydroperoxide forms, the lithium compounds are confined to lithium peroxide Li_2O_2 and the compound that it forms with hydrogen peroxide and water, the structure of which has been the subject of dispute in the literature. It has not yet been found possible to prepare lithium peroxide by the action of oxygen at high pressure and temperature on metallic lithium [1], lithium oxide [2], or lithium hydroxide [3].

The principal method for the preparation of Li_2O_2 is that of de Forcrand [1], which consists in the action of hydrogen peroxide on an aqueous-alcoholic solution of lithium hydroxide. Under these conditions de Forcrand obtained a compound of composition $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, which yielded anhydrous Li_2O_2 when vacuum-dried over P_2O_5 for four weeks. According to Pierron [4] and Winternitz [5], lithium peroxide can be prepared directly in the anhydrous form by the action of hydrogen peroxide on lithium hydroxide in a medium of boiling alcohols. In 1952 Cohen [6] prepared a peroxide compound of lithium by the action of hydrogen peroxide on lithium ethoxide, and he characterized it as a compound of the hydroperoxide type and assigned it the formula $LiOOH \cdot H_2O$. Cohen denies the existence of perhydrate forms of lithium peroxide ($Li_2O_2 \cdot xH_2O_2 \cdot y\,H_2O$).

Thompson and Kleinberg [7] consider that a higher lithium peroxide LiO_2 exists. By rapid oxidation of a solution of lithium in liquid ammonia at −78° they succeeded in obtaining a lemon-yellow precipitate, the absorption spectrum of which was found to be analogous to the absorption spectra of the higher peroxides of sodium and potassium, but there has been no further confirmation of the existence of the compound LiO_2. According to the X-ray investigations of Feher [8], Aguzzi and Genoni [9], and Cohen [6], Li_2O_2 crystallizes in the tetragonal syngony. In later work Feher [10] considers that it crystallizes in the hexagonal syngony. The density of Li_2O_2 is d^{25} 2.26 according to Cohen [6] and d^{20} 2.297 according to Feher [10].

The properties of the compounds $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $LiOOH \cdot H_2O$ or $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ have received little study. In spite of de Forcrand's work, Cohen and Feher deny the existence of the first compound. According to Cohen [6], $LiOOH \cdot H_2O$ crystallizes in the rhombic syngony and has a density of d^{25} 1.69.

EXPERIMENTAL

Experimental Procedure

In order to resolve the question of the actual composition and nature of the peroxide compounds of lithium we have undertaken a systematic study of the solubility isotherms of the ternary system LiOH – H_2O_2 – H_2O, in which we have determined the compositions of the solid phases by the residue method at +10°, 0°, −10°, and −21°. As starting materials we used $LiOH \cdot H_2O$ free from Li_2CO_3, which was prepared by the action of water on lithium in an atmosphere of hydrogen, and concentrated hydrogen peroxide freed from stabilizers by vacuum distillation in a laboratory apparatus.

For the determination of the solubility isotherms, constant temperature was attained with the aid of a thermostat consisting of a one-liter Dewar vessel mounted in a ten-liter Dewar vessel. A thermostat of this construction was found to maintain a temperature constant within 0.3-0.5° for not less than four hours, which was quite long enough for the establishment of equilibrium in the system LiOH – H_2O_2 – H_2O. Cooling to the required temperature was carried out with water (+10°), ice (0°), a 3 : 7 mixture of KCl and ice (−10°), or a mixture of NaCl and ice (−21°).

Samples were taken in a vessel consisting of a test tube with an exit tube in which a funnel carrying a No. 3 glass filter was fixed with the aid of a rubber stopper. When the samples were taken, this vessel was placed in a Dewar vessel containing a suitable cooling mixture.

The liquid phase and the solid residue were analyzed for their contents of active oxygen and Li_2O. Weighed samples for active-oxygen determination were first stabilized in a saturated solution of boric acid, and active oxygen was subsequently determined by titration with 0.1 N $KMnO_4$ in presence of H_2SO_4. Weighed samples for Li_2O determination were transferred with the aid of water into conical flasks and boiled for 10-15 minutes to destroy H_2O_2, after which Li_2O was determined by titration to phenolphthalein with 0.1 N H_2SO_4.

For each temperature a preliminary determination was made by the graphical method of the time required for the establishment of equilibrium (from the constancy of the active-oxygen content of the liquid phase). It was found that in the system $LiOH - H_2O_2 - H_2O$ at temperatures in the range +10° to −21° equilibrium is attained, for practical purposes, within 1.5-2 hours.

Data for the Construction of the Solubility Isotherms of the Ternary System $LiOH - H_2O_2 - H_2O$

Data for the construction of the +10°, 0°, −10°, and −21° solubility isotherms of the system $LiOH - H_2O_2 - H_2O$ are given in Tables 1-4 and are represented graphically on diagrams in Figures 1-4, and also in rectangular coordinates in Figures 5-8, in which the H_2O_2 content is plotted as abscissas and the Li_2O content as ordinates (as percent in the liquid phase).

The +10°, 0°, −10°, and −21° isotherms indicate the existence of the following solid phases: $LiOH \cdot H_2O$, $H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $Li_2O_2 \cdot 2H_2O_2$ (the solid phase $LiOH \cdot H_2O$ is absent at −21°).

The −21° isotherm is bounded by a region of frozen solutions in the H_2O_2 concentration range of 0-20.69%.

For the other temperatures studied, the region of existence of the solid phase $LiOH \cdot H_2O$ corresponds to the following ranges of H_2O_2 concentration in the liquid phase:

Temperature	+10°	0°	−10°
Concentration of H_2O_2 in the liquid phase (% by weight)	0−4.78	0−4.59	0−4.57

The most interesting solid phases of the system are the compounds of the peroxide type $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, and the compound $Li_2O_2 \cdot 2H_2O_2$, which has not been reported previously.

TABLE 1

Solubility Data for the system $LiOH - H_2O_2 - H_2O$ at 10°

Point No.	Composition of liquid phases (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	0.5 O_2	H_2O_2	Li_2O	H_2O	0.5 O_2	Li_2O	H_2O	
26	0.97	2.06	7.03	92.00	0.26	32.50	67.24	$LiOH \cdot H_2O$
27	1.78	3.78	7.27	90.95	0.54	27.88	71.58	Ditto
9	2.06	4.38	7.33	90.61	2.56	31.34	66.01	Ditto
24	2.25	4.78	8.07	89.68	7.42	28.64	63.94	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
18	2.20	4.68	7.69	90.11	9.79	15.31	74.90	Ditto
8	2.44	5.19	7.27	90.29	7.84	10.83	81.33	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
1	3.34	7.10	3.92	92.74	20.71	20.55	58.74	Ditto
6	3.20	8.29	3.35	92.75	17.62	15.45	66.93	Ditto
20	4.30	9.14	3.56	92.14	16.21	15.30	68.59	Ditto
3	7.33	15.58	4.04	88.63	22.25	22.54	55.21	Ditto
23	12.40	26.36	4.55	83.05	30.91	18.17	60.92	Ditto
4	14.54	0.91	4.92	80.54	24.77	22.08	53.15	Ditto
25	19.65	41.78	5.57	74.78	23.10	19.27	57.36	Ditto
7	19.14	40.69	5.48	75.38	23.31	15.13	61.56	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
13	20.52	43.63	5.47	74.01	23.85	16.59	59.56	Ditto
5	22.32	47.45	5.56	72.12	26.66	20.45	52.89	Ditto
11	24.18	51.41	5.62	70.20	25.96	15.78	58.26	Ditto
28	26.48	56.30	5.94	67.58	26.81	19.38	59.81	Ditto
16	27.55	58.57	6.02	66.43	27.56	15.56	56.88	Ditto
29	26.91	57.21	5.81	67.28	29.30	16.08	54.62	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O + Li_2O \cdot 2H_2O_2$
15	27.48	58.42	5.55	66.97	35.15	15.41	49.44	$Li_2O_2 \cdot 2H_2O_2$
22	27.53	58.53	5.68	66.79	40.07	15.49	44.44	Ditto
17	30.30	64.42	5.16	64.54	36.75	12.17	51.08	Ditto
10	30.50	64.84	5.00	64.50	37.50	12.27	50.23	Ditto

TABLE 2

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at 0°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	0.5 O_2	H_2O_2	Li_2O	H_2O	0.5 O_2	Li_2O	H_2O	
19	1.49	3.17	7.38	91.13	0.36	30.51	69.13	$LiOH \cdot H_2O$
16	1.75	3.72	7.22	91.03	0.51	30.03	69.46	Ditto
15	2.13	4.53	7.42	90.35	1.36	32.47	66.17	Ditto
21	2.16	4.59	7.30	90.54	7.26	13.47	79.27	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
20	3.82	8.12	4.18	92.00	9.89	9.12	80.99	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
24	3.57	7.59	3.59	92.84	11.89	11.87	76.24	Ditto
1	6.43	13.67	3.85	89.72	21.89	19.59	58.52	Ditto
26	11.11	23.62	4.33	84.56	20.60	14.57	64.83	Ditto
29	14.93	31.74	4.76	80.31	24.73	21.73	53.54	Ditto
2	17.69	37.61	5.05	77.26	24.12	19.70	56.18	Ditto
14	18.79	39.95	5.07	76.14	23.60	18.52	57.88	Ditto
30	18.41	39.14	5.19	76.40	25.22	19.59	55.19	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
13	19.37	41.18	4.18	76.45	24.78	18.78	56.44	Ditto
7	20.74	44.09	4.68	74.58	25.15	19.25	55.60	Ditto
12	22.06	46.90	4.27	73.67	26.33	19.35	54.32	Ditto
25/2	24.21	52.96	6.12	68.97	26.66	17.77	55.57	Ditto
11	25.44	54.09	4.52	70.04	26.44	17.66	55.90	Ditto
3	25.46	54.13	5.94	68.60	28.70	17.54	53.76	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O + Li_2O_2 \cdot 2H_2O_2$
8	25.86	54.98	4.80	69.34	32.43	16.83	49.74	$Li_2O_2 \cdot 2H_2O_2$
9	27.39	58.23	5.00	67.61	38.62	15.66	52.48	Ditto
23	29.36	62.42	4.97	65.67	37.05	13.94	49.90	Ditto
28	31.31	66.57	3.70	64.99	37.59	13.88	48.53	Ditto
10	32.33	68.73	3.19	64.48	40.13	15.52	44.35	Ditto

TABLE 3

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at −10°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	0.5 O_2	H_2O_2	Li_2O	H_2O	0.5 O_2	Li_2O	H_2O	
2	1.49	3.17	7.31	91.20	1.67	31.34	66.99	$LiOH \cdot H_2O$
1	2.15	4.57	7.80	90.05	2.44	22.75	74.31	Ditto
18	1.98	4.21	7.76	90.26	4.88	22.00	73.12	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
7	2.34	4.97	7.05	90.61	8.99	20.94	70.07	Ditto
22	2.37	5.04	5.08	92.55	12.25	13.78	73.97	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
8	2.54	5.40	5.68	91.78	12.29	13.25	74.46	Ditto
3	4.50	9.57	3.42	92.08	16.40	14.93	68.67	Ditto
4	9.38	19.94	4.20	86.42	17.95	15.21	66.86	Ditto
5	14.51	30.85	4.81	80.68	21.31	17.46	61.23	Ditto
6	17.29	36.76	4.91	77.80	21.92	16.12	61.96	Ditto
11	18.68	39.71	4.77	76.55	21.19	14.92	63.89	Ditto
13	18.95	40.29	5.02	76.03	23.06	14.99	61.95	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O + Li_2C \cdot H_2O \cdot 2H_2O$
9	22.00	46.47	5.25	72.75	24.85	17.33	57.82	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
19	24.05	51.13	5.37	70.58	26.83	19.71	53.46	Ditto
10	25.61	54.45	5.59	68.80	28.19	18.63	53.18	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O + Li_2O_2 \cdot 2H_2O_2$
14	25.32	53.83	5.64	69.04	34.06	14.45	51.49	$Li_2O_2 \cdot 2H_2O_2$
12	28.75	61.12	4.58	66.67	39.17	18.13	42.70	Ditto
21	30.55	64.95	3.92	65.53	36.74	12.26	51.00	Ditto
20	35.59	75.66	2.38	62.03	40.75	11.54	47.71	Ditto

TABLE 4

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at − 21°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	0.5 O_2	H_2O_2	Li_2O	H_2O	0.5 O_2	Li_2O	H_2O	
15	10.80	22.96	4.29	84.91	–	–	100	Ice
6	9.73	20.69	3.85	86.42	17.43	13.24	69.33	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
1	13.13	27.91	4.44	82.43	19.87	16.00	64.13	Ditto
12	17.06	36.27	5.09	77.85	23.52	20.28	56.20	Ditto
14	17.95	38.16	5.14	76.91	23.71	18.76	57.53	Ditto
2	17.47	37.14	4.95	77.58	24.11	18.42	57.47	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
17	18.86	40.10	5.00	76.14	22.59	15.31	61.60	Ditto
16	22.94	48.77	5.12	71.94	24.60	12.53	62.87	Ditto
8	24.62	52.34	5.34	70.04	25.47	16.61	67.92	Ditto
9	26.05	55.32	5.31	68.64	27.13	12.41	60.46	Ditto
3	25.51	54.23	5.43	69.06	37.75	15.54	46.17	$Li_2O_2 \cdot 2H_2O_2$
10	26.85	57.08	6.13	67.02	34.42	12.07	53.51	Ditto
22	27.59	58.66	4.08	68.33	33.63	13.05	53.32	Ditto
21	27.90	59.32	4.01	68.09	38.10	16.37	45.53	Ditto
11	31.18	66.29	4.69	64.13	35.67	10.17	54.16	Ditto
19	31.89	67.80	2.76	65.35	39.61	12.49	47.90	Ditto
4	34.09	72.43	3.53	62.38	36.60	10.01	53.29	Ditto
18	39.49	83.96	2.24	58.27	40.38	8.81	50.81	Ditto

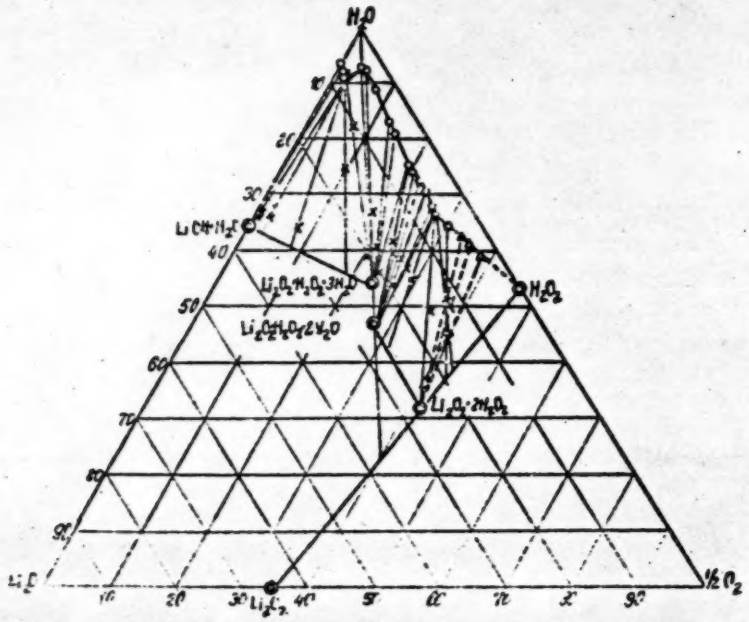


Fig. 1. + 10° isotherm of the system $LiOH - H_2O_2 - H_2O$

As the temperature is lowered, the field of existence of the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ becomes smaller. The field of existence of the solid phase $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ is at a minimum at − 10°. When the temperature is raised to 0° and + 10°, and also when it is lowered to − 21°, this field of existence grows somewhat larger. The solid phase $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ is least soluble at 0° (4.18-4.80% Li_2O in the liquid phase).

The diagrams in Figures 5-8 are all characterized by the presence of two clearly defined curves corresponding to the two phases $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$.

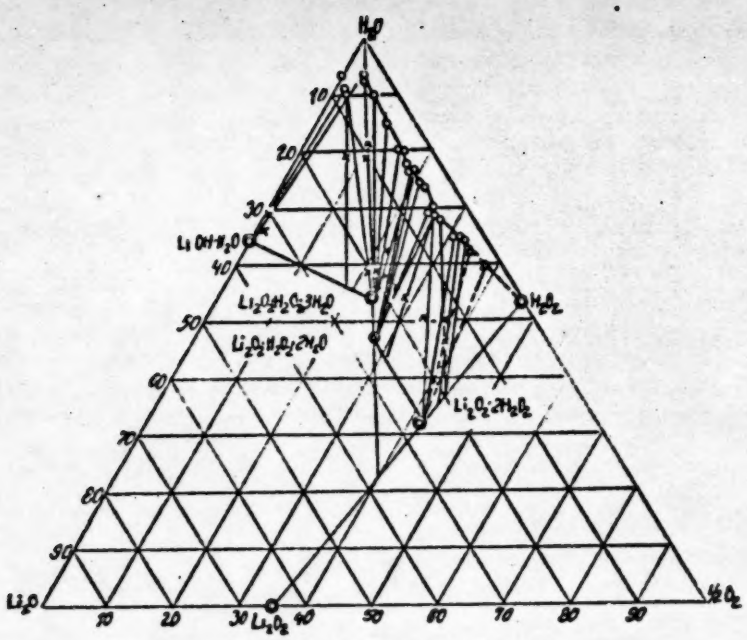


Fig. 2. 0° isotherm of the system $LiOH - H_2O_2 - H_2O$

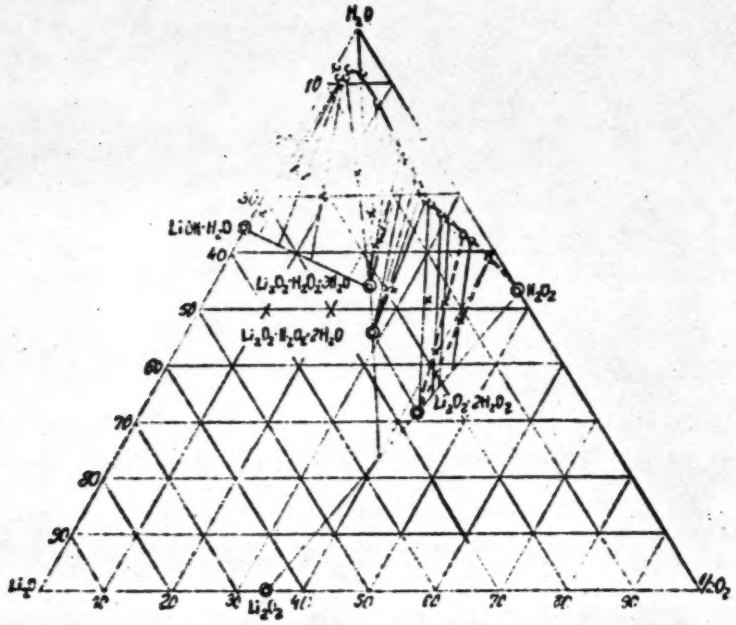


Fig. 3. −10° isotherm of the system $LiOH - H_2O_2 - H_2O$

Hence, in spite of Cohen's assertions to the contrary, we may conclude that the compounds $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ exists.

As the temperature is lowered, the field of existence of the compound $Li_2O_2 \cdot 2H_2O_2$ becomes larger. Whereas at 10° this compound exists over a range of only 6.27% H_2O_2 (58.57-64.84% H_2O_2 in the liquid phase), at −21° its field ranges over 26.88% H_2O_2 (57.08-83.96% H_2O_2 in the liquid phase).

In the field of high H_2O_2 concentrations in the liquid phase, much decomposition occurs. Hence, the tie lines joining the liquid-phase and solid-residue compositions in the diagrams of Figures 1-4 are displaced to the right of the figurative point corresponding to the solid phase $Li_2O_2 \cdot 2H_2O_2$. The directions in which these tie lines

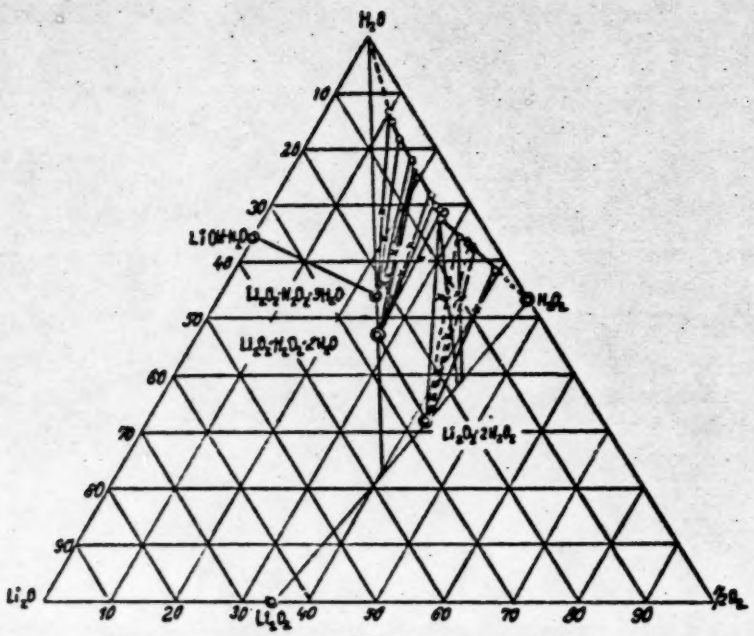


Fig. 4. −21° isotherm of the system $Li_2O_2-H_2O_2-H_2O$

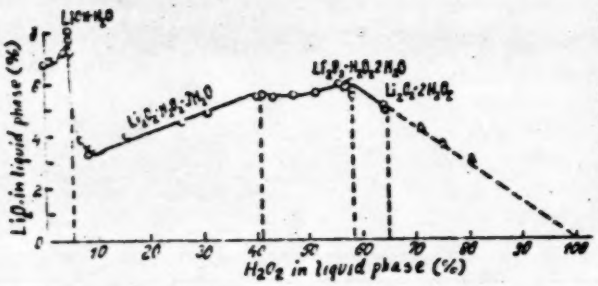


Fig. 5. +10° isotherm of the system $LiOH-H_2O_2-H_2O$

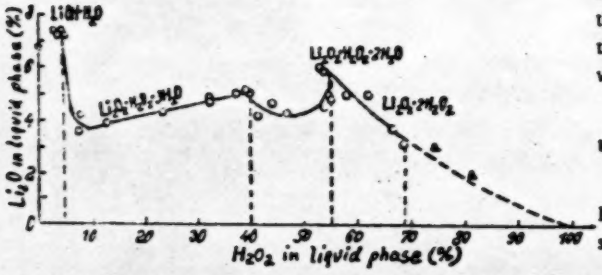


Fig. 6. 0° isotherm of the system $LiOH-H_2O_2-H_2O$

should have gone are shown on the Gibbs triangles (Figures 1-4) by broken lines.

On the basis of the solubility data for the system $LiOH-H_2O_2-H_2O$ at +10°, 0°, −10°, and −21°, a polythermal diagram was constructed (Fig. 9). There are seven fields in this diagram. The broken lines indicate the parts of the system that we have not investigated. The curve for the freezing of H_2O_2 was plotted from the data of Mironov and Befgman [11].

It was found that $LiOH \cdot H_2O$ is more active in decomposing H_2O_2 than $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$. Hence, in the fields of high H_2O_2 concentrations, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ was used as starting material. In the diagram for the −21° isotherm in Fig. 8 the broken line shows the composition of the liquid phase corresponding to the equilibrium state for the case in which $LiOH \cdot H_2O$ was used as starting material.

Under these conditions, for the same Li_2O content in the liquid phase, the H_2O_2 content is less.

We isolated the solid phases of the system $LiOH-H_2O_2-H_2O$ and studied them by the methods of physicochemical analysis.

SUMMARY

1. The ternary system $LiOH-H_2O_2-H_2O$ was studied by the solubility method at +10°, 0°, −10°, and −21°, and solubility isotherms and polytherms were plotted for the system for the temperature range +10° to −21°.

2. A solubility study of the ternary system $LiOH-H_2O_2-H_2O$ in which the compositions of solid phases were determined by the residue method has established the existence of the following peroxide compounds of lithium: $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $Li_2O_2 \cdot 2H_2O_2$.

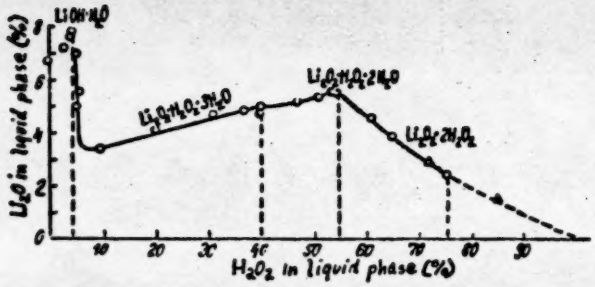


Fig. 7. $-10°$ isotherm of the system $LiOH - H_2O_2 - H_2O$

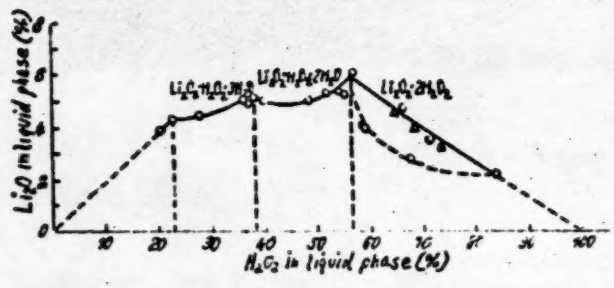


Fig. 8. $-21°$ isotherm of the system $LiOH - H_2O_2 - H_2O$

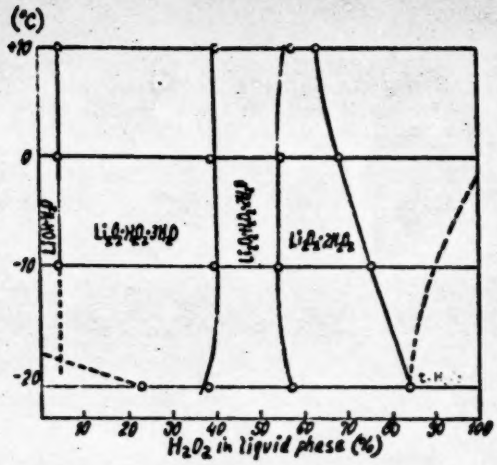


Fig. 9. Polythermal diagram showing the limits of existence of the solid phases in saturated solutions of the ternary system $LiOH - H_2O_2 - H_2O$

3. Cohen's assertion regarding the absence of the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, previously found by de Forcrand, was not confirmed.

The compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ exists over a wide range of temperature and over a wide range of hydrogen peroxide concentrations (5.0-40.0% H_2O_2).

4. The existence of the previously unknown compound $Li_2O_2 \cdot 2H_2O_2$ was established; it is stable at H_2O_2 concentrations in the liquid phase of more than 50%. The upper limit of the stability of $Li_2O_2 \cdot 2H_2O_2$ is at a hydrogen peroxide concentration in the liquid phase of 64.8% at $+10°$ and 84.0% at $-21°$.

5. The solid phases isolated in the course of the study of this system were investigated by several physicochemical methods.

LITERATURE CITED

[1] R. deForcrand, Comptes rend. 130, 1465 (1900).

[2] J. Milbauer, Chem. 40, 587 (1916).

[3] F. Fischer, H. Ploetze, Z. anorg Chem. 75, 30(1912).

[4] P. Pierron, Bull. Soc. Chim. 6, 235 (1939).

[5] P. Winternitz, U.S. Pat. 2488485, Nov. 1949.

[6] A. J. Cohen, J. Am. Chem. Soc. 74, 3762 (1952).

[7] J. K. Thompson, J. Kleinberg, J. Am. Chem. Soc. 73, 1243(1951).

[8] F. Feher, Ang. Chem. 51, 497 (1938).

[9] A. Aguzzi, F. Genoni, Gazz. chim. Ital. 68, 816 (1938).

[10] F. Feher, Ber. 11, 1389 (1953).

[11] K. E. Mironov and A. G. Bergman, Proc. Acad. Sci. USSR 81, 6, 1081 (1951).

Received July 26, 1954

N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences

BLANK
PAGE

EQUATION FOR THE DIFFUSION CURRENT AT A DROPPING ELECTRODE TAKING INTO ACCOUNT THE SCREENING OF PART OF THE ELECTRODE SURFACE

S. G. Mairanovsky and M. B. Neiman

In the derivation of the equation for the diffusion current in polarography the fact that part of the dropping mercury electrode is screened by the surface of the tip of the capillary is neglected. In the present paper an estimate is made of the effect of this screening on the value of the limiting diffusion current.

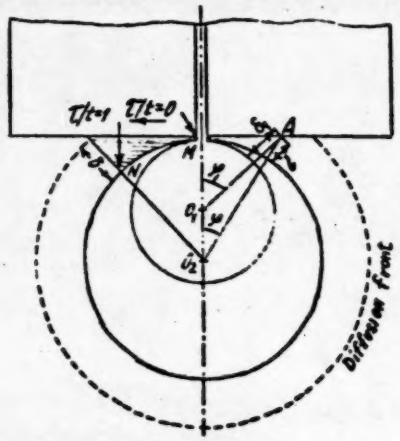


Fig. 1. Diagram for calculation of the screening effect (the left half of the screened space is shaded).

Let is be supposed that the diffusion front, extending from the surface of the electrode into the solution, reaches a point A on the surface of the tip (Fig. 1) at time $t = \tau$. The variation in the concentration of the depolarizer at this point as further time elapses will be expressed by the relation (the effect of the sphericity of the dropping electrode [1, 2] being neglected):

$$\frac{c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2}. \qquad (1)$$

(D is the diffusion coefficient of the depolarizer and x is the distance from the surface of the drop).

In order to simplify the calculation we shall apply the concept of a conventional thickness of diffusion layer [3], equal in this case to

$$\delta = \sqrt{\pi D t}.$$

The value of $\partial c_A/\partial x$ at A is close to zero [4], but at the electrode surface it is c_A/l [3] (l is the distance of the point A from the surface of the drop), so that the second derivative of concentration with respect to distance can be approximately expressed as

$$\frac{\partial^2 c_A}{\partial x^2} \approx -\frac{c_A}{l^2}, \text{ so that}$$

$$\left(\frac{c_A}{\partial t}\right)_A \approx -D\frac{c_A}{l^2}. \qquad (2)$$

The introduction of this approximation, as will be seen later, does not affect the final results to an appreciable extent.

At $t = \tau$ the distance l is equal to the thickness of the diffusion layer δ; as time proceeds it diminishes owing to the growth of the drop. An examination of Fig. 1 indicates that

$$l = \frac{r(1-\cos\varphi)}{\cos\varphi} = \frac{2r\sin^2\frac{\varphi}{2}}{\cos\varphi}, \qquad (3)$$

(r is the radius of the drop).

At low values of φ_1, for which

$$\varphi_1 \approx \sin\varphi_1 \ (4) \text{ and } \cos\varphi_1 \approx 1, \qquad (5)$$

we may write, on the basis of Equation 3:

$$l/l_1 = \frac{r_1}{r} = \left(\frac{t_1}{t}\right)^{1/2}. \qquad (6)$$

Assuming that $t_1 = \tau$, we obtain from Equation 6:

$$l = \delta\left(\frac{\tau}{t}\right)^{1/2}. \qquad (7)$$

After substituting for $\underline{1}$ from Equations 7 and 2, we obtain:

$$\left(\frac{\partial c_A}{\partial t}\right)_A = -D\,\frac{c_A t^{2/3}}{\delta^2 \tau^{2/3}}\,. \tag{8}$$

which yields, after separation of variables and integration between the limits of τ and t ($\tau \leq t$):

$$\ln\frac{c_A}{c_0} = -\tfrac{2}{3}D\,\frac{t^{5/3}-\tau^{5/3}}{\delta^2\tau^{2/3}}\,, \tag{9}$$

(c_0 is the concentration in the mass of the solution).

After substitution of the value $\delta^2 = {}^3/_7\pi D\tau$ in Equation 9 and rearrangement, we obtain for c_A:

$$c_A = c_0 e^{-7/3\pi\left[\left(\frac{t}{\tau}\right)^{5/3}-1\right]}. \tag{10}$$

For the concentration gradient at the surface of the drop opposite to the point $\underline{A}$ we may write:

$$\left(\frac{\partial c_A^{scr.}}{\partial x}\right)_{x=0} \approx \frac{c_A}{\underline{1}} = \frac{c_A t^{1/3}}{\tau^{1/3}\,3/7\,\pi D\tau}\,. \tag{11}$$

The concentration gradient at the unscreened surface (the effect of sphericity being neglected) is [4]

$$\left(\frac{\partial c}{\partial x}\right)_{x=0}^{unscr.} = \frac{c_0}{\sqrt{3/7\,\pi D\tau}}\,. \tag{12}$$

From Equations 10, 11, and 12 it follows that

$$\left(\frac{\partial c_A}{\partial x}\right)_{x=0}^{scr.} : \left(\frac{\partial c}{\partial x}\right)_{x=0}^{unscr.} = \frac{t^{5/6}}{\tau^{5/6}}\,e^{\frac{7}{5\pi}\left[\left(\frac{t}{\tau}\right)^{5/3}-1\right]}. \tag{13}$$

We now introduce a new variable $y = \tau/t$, varying at a given moment of time from 0 to 1 along the arc $\underline{M}$ (Fig. 1). The graph for the dependence of the ratio of concentration gradients on $\underline{y}$ for an arbitrary moment of time is given in Fig. 2. The mean instantaneous value of the ratio of gradients over the whole of the screened surface is given by:

$$\left[\left(\frac{\partial c}{\partial x}\right)^{scr.}_{x=0} \Big/ \left(\frac{\partial c}{\partial x}\right)^{unscr.}_{x=0}\right]_{mean} = \int_{y=0}^{y=1} y^{-5/6}\,e^{-\frac{7}{5\pi}(y^{-5/3}-1)}\,dy = \underline{M}. \tag{14}$$

It follows from Equation 14 that the value of $\underline{M}$, at least on the simplifying assumptions made, is independent of time and has the value of about 0.554 (graphical integration). It may therefore be considered that the mean current density at the screened parts of the surface of the drop are little more than half of the corresponding values for the unscreened parts.

Let us derive the expression for the total current. It follows from an examination of Fig. 1 that the screened surface is

$$S_{scr.} = 2\pi r^2\,\frac{\sqrt{3/7\,\pi Dt}}{r+\sqrt{3/7\,\pi Dt}}\,. \tag{15}$$

For short periods of dropping $r \gg \sqrt{3/7\,\pi Dt}$, and Equation 15 may be expressed in the form: (15)

$$S_{scr.} \approx 2\pi r\sqrt{3/7\,\pi Dt}\,. \tag{16}$$

The expression for the current taking into account the corrections for the sphericity of the electrode [1, 2] and the reduced current density in the screened regions has the form:

$$i = nFDc_0\left(4\pi r^2 - 2\pi r_1\sqrt{3/7\,\pi Dt}\right)\left(\frac{1}{\sqrt{3/7\,\pi Dt}} + \frac{1}{r}\right) + 2\pi r\sqrt{3/7\,\pi Dt}\cdot nFDc_0 M\left(\frac{1}{\sqrt{3/7\,\pi Dt}} + \frac{1}{r}\right). \tag{17}$$

The first member of the expression is the component of the current at the unscreened surface, and the second is the component at the screened surface. After rearrangement, Equation 17 takes the form:

$$i = nFDc_0\cdot 4\pi r^2\left(\frac{1}{\sqrt{3/7\,\pi Dt}} + \frac{1}{r}\right)\left[1 - \frac{\sqrt{3/7\,\pi Dt}}{2r}(1-M)\right]. \tag{18}$$

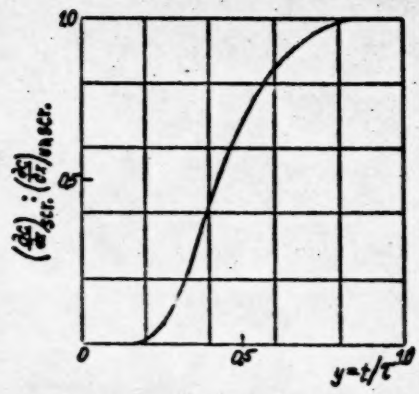


Fig. 2. Dependence on $\underline{y}$ of the ratio of concentration gradients at the screened and unscreened parts of the surface (for a given value of $\underline{\tau}$)

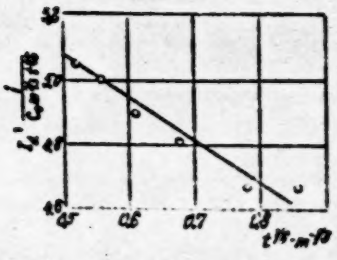


Fig. 3. Dependence of the diffusion-current constant on $t^{1/6}\ m^{-1/3}$ for a capillary working with a blade. 2.07-millimolar solution, $\underline{h}$ = 40 cm, $\underline{M}$ = 2.25, $\underline{\tau}$ = 0.512 sec.

Substituting the value $\underline{\tau} = 0.026(mt)^{1/3}$, in Equation 18, opening the square brackets, and integrating over the time t_0 required for the formation of a drop, we obtain for the average current:

$$\bar{I} = 607nD^{1/2}c_0m^{2/3}t^{1/6}[1 + 39(mt_0)^{-1/3}(Dt_0)^{1/2} - 8.7(mt_0)^{-1/3}(Dt_0)^{1/2} - 35(mt_0)^{-2/3}Dt_0]. \qquad (19)$$

In considering the phenomena occurring at the screened surface, we did not take into account the fact that the concentration of depolarizer at the tip of the capillary, which is reduced during the growth of the drop, will not regain the value c_0 (the concentration in the mass of the solution) after the drop has broken away. The effect of this will be to reduce the value of $\underline{M}$, in comparison with the value given by Equation 14, and to increase the effective screening surface.

The magnitude of this effect depends mainly on the area of the tip of the capillary and the agitation given to the solution when the drop breaks away, i.e. is determined solely by the properties of the given capillary. The displacement of impoverished solution from the screened space during the growth of the mercury drop has a similar effect. In order to take these factors into account, a correction coefficient $\underline{B} \geq 1$ must be introduced in front of the second member within the square brackets in Equation 18, and the value of $\underline{B}$ will be different for different capillaries. The value of $\underline{B}$ is particularly high for capillaries working with a blade which effects forced breakaway of the drop [5] and which greatly increases the screened surface. Results of experiments with such a capillary are shown in Fig. 3; for this capillary the value of $\underline{B}$ was found to be about 6.

Another possible case arises when the outside of the capillary is tapered at the tip. The area of the tip is then reduced, and the screened surface is also reduced. In this case $\underline{B}$ may be less than unity. Finally, therefore, we have:

$$\bar{I} = 607nD^{1/2}c_0m^{2/3}t_0^{1/6}[1 + 39\ m^{-1/3}t_0^{1/6}D^{1/2} - B(8.7m^{-1/3}t_0^{1/6}D^{1/2} + 35\ m^{-2/3}t_0^{1/3}D)]. \qquad (20)$$

In our opinion, only variation in the value of $\underline{B}$ for different capillaries can explain the large discrepancies found experimentally by various workers in the numerical values of the coefficient $\underline{A}$ in front of the correction term of the corrected Ilkovic equation [1, 2, 6, 7].

The effect of screening can explain also the reduction in the diffusion-current constant at a low rate of dropping. This phenomenon was first pointed out by L. and T. Meites [6], who, however, could not explain it. It can be seen from Equation 19 that the last correction member is most dependent on t_0 (mt_0 is constant for a given capillary), but its value becomes appreciable only for high values of t_0. In order to take this relationship into account, Equation 15 should be used in place of 16, account being taken of the fact that at high values of t_0 the conditions expressed in Equations 4 and 5 will not apply exactly, and this will affect the value of $\underline{M}$. This does not affect, however, the general course of the relation of the diffusion-current constant to t_0 *.

* After the present work was finished we became acquainted with a paper by Matsuda [8], which also takes account of screening, attributing it to the effect of reduction in the volume of the diffusion layer due to the presence therein of the end of the capillary. According to Matsuda, the effect of screening for all capillaries is to reduce the correction member for sphericity by a factor of 1.54, without change of sign.

SUMMARY

1. An estimate is made of the effect of the screening of the dropping electrode on the value of the diffusion current.

2. It is shown that screening of part of the electrode surface results in a reduction in the correction coefficient for sphericity in the corrected Ilkovic equation.

3. The lack of accord in the values foundby various authors for the correction coefficient taking into account the sphericity of the electrode – both among themselves and also with the theoretically deduced values – is explained by differences in the extent of the screening of the electrode.

4. Lowering of the diffusion-current constant at a low rate of dropping is explained by an increase in the extent of screening.

LITERATURE CITED

[1] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc. 72, 438 (1950).

[2] H. Strehlow and M. Stackelberg Z. Elektochem. 54, 51 (1950).

[3] S. Glasstone, Introduction to Electrochemistry, Foreign Lit. Press, 1951, p. 578.

[4] A. N. Frumkin, V. S. Bagotsky, Z. A. Iofa, and V. N. Kabanov, Kinetics of Electrode Processes, Moscow State Univ. Press, Moscow, 1952, p. 87.

[5] E. M. Skobets and N. S. Kavetsky, Factory Labs; 15, 1299 (1949).

[6] L. Meites and T. Meites, J. Am. Chem. Soc. 73, 395 (1951).

[7] W. Hans and W. Jensch, Z. Elektrochem. 56, 648 (1952).

[8] H. Matsuda, Bull. 26, 342 (1953).

Received July 29, 1954

Institute of Chemical Physics of the
USSR Academy of Sciences

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 6. DIESTERS OF 2-ISOPROPOXY-, 2-ISOBUTOXY-, AND 2-ISOPENTYLOXY-VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

In a previous communication we have described diesters of 2-alkoxyvinylphosphonic acids prepared by the action of alcohols on 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic dichlorides in presence of pyridine [1].

We decided that, in order to make a more extensive and thorough investigation of these interesting compounds, we should carry out the synthesis of diesters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids.

For the preparation of these compounds we used the method described previously, and we obtained the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids.

The compounds so obtained are colorless liquids, readily distilled under reduced pressure, and capable of being preserved unchanged for a long time. All of the esters are soluble in the usual organic solvents; only the dimethyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters are soluble in water. The diallyl esters polymerize in presence of peroxides, and they will copolymerize with methyl methacrylate and other unsaturated compounds. Physical properties of the compounds obtained are given in Tables 1-3.

TABLE 1

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$i\text{-}C_3H_7 - O - CH = CHPO(OCH_3)_2$	94 – 95 (2)	1.4438	1.1042
$i\text{-}C_3H_7 - O - CH = CHPO(OC_2H_5)_2$	103 (1)	1.4428	1.0450
$i\text{-}C_3H_7 - O - CH = CHPO(O - C_3H_7\text{-}n)_2$	113 (1)	1.4439	1.0141
$i\text{-}C_3H_7 - O - CH = CHPO(O - C_3H_7\text{-}i)_2$	99 (2)	1.4360	0.9973
$i\text{-}C_3H_7 - O - CH = CHPO(O - C_4H_9\text{-}n)_2$	132 – 133 (2)	1.4460	0.9910
$i\text{-}C_3H_7 - O - CH = CHPO(O - C_4H_9\text{-}i)_2$	116 (1)	1.4440	0.9847
$i\text{-}C_3H_7 - O - CH = CHPO(OC_5H_5)_2$	120 (2)	1.4651	1.0448
$i\text{-}C_3H_7 - O - CH = CHPO(OC_6H_{13}\text{-}n)_2$	149 (2)	1.4498	0.9628
$i\text{-}C_3H_7 - O - CH = CHPO(OCH_2 - CH_2 - OCH_3)_2$	155 (3)	1.4555	1.1002
$i\text{-}C_3H_7 - O - CH = CHPO(O - CH_2 - CH_2 - OC_2H_5)_2$	155 (1)	1.4520	1.0652

TABLE 2

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$i\text{-}C_4H_9 - O - CH = CHPO(OCH_3)_2$	105 (2)	1.4487	1.0831
$i\text{-}C_4H_9 - O - CH = CHPO(OC_2H_5)_2$	110 (2)	1.4435	1.0310
$i\text{-}C_4H_9 - O - CH = CHPO(OC_3H_7\text{-}n)_2$	124 (2)	1.4442	1.0014
$i\text{-}C_4H_9 - O - CH = CHPO(OC_3H_7\text{-}i)_2$	120 (2)	1.4405	0.9948
$i\text{-}C_4H_9 - O - CH = CHPO(OC_4H_9\text{-}n)_2$	144 (1)	1.4470	0.9849
$i\text{-}C_4H_9 - O - CH = CHPO(OC_4H_9\text{-}i)_2$	135 (2)	1.4440	0.9804
$i\text{-}C_4H_9 - O - CH = CHPO(OC_5H_5)_2$	130 (1)	1.4643	1.0417
$i\text{-}C_4H_9 - O - CH = CHPO(OC_6H_{13}\text{-}n)_2$	165 (1)	1.4498	0.9597
$i\text{-}C_4H_9 - O - CH = CHPO(OCH_2 - CH_2 - OCH_3)_2$	163 (2)	1.4543	1.0900
$i\text{-}C_4H_9 - O - CH = CHPO(OCH_2 - CH_2 - OC_2H_5)_2$	170 (2)	1.4509	1.0533

TABLE 3

Formula of Compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	109.5 (1)	1.4508	1.0667
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	119 (1)	1.4464	1.0928
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	132 (1)	1.4482	0.9960
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	120 (2)	1.4418	0.9866
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$	148 (1)	1.4490	0.9896
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	145 (2)	1.4458	0.9734
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	137 (1)	1.4645	1.0335
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(O-C_6H_{13}\text{-}n)_2$	171 (1)	1.4500	0.9618
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	173 (1)	1.4550	1.0758
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	179 (1)	1.4527	1.0453

EXPERIMENTAL

Diesters of 2-Isopropoxyvinylphosphonic Acid

Dimethyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OCH_3)_2$. A mixture of 3.2 g of methyl alcohol, 7.9 g of dry pyridine, and 60 ml of dry benzene was introduced into a three-necked flask provided with stirrer, dropping funnel, and reflux condenser protected by a calcium chloride tube. With thorough cooling and stirring 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added, and after the addition was complete the reaction mixture was heated for about one hour in a water bath. The precipitate was filtered off, and the filtrate was treated with saturated sodium carbonate solution and then dried with calcined sodium sulfate. Benzene was distilled off from a water bath and the residue was vacuum-distilled. A second distillation yielded 6 g (62%) of a substance having b.p. 94-95° (2 mm); d_4^{20} 1.1042; n_D^{20} 1.4438

	Found %:	C 43.04; 42.96; H 8.09; 8.00
$C_7H_{15}O_4P$.	Calculated %:	C 43.29; H 7.73

The other diesters of 2-isoalkoxyvinylphosphonic acids were prepared by the method described above.

Diethyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_2H_5)_2$. Reaction between 4.6 g of absolute ethyl alcohol, 7.9 g of pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 8.5 g of a substance having b.p. 103° (1 mm); d_4^{20} 1.0450; n_D^{20} 1.4428

	Found %:	C 48.50; 48.38; H 8.44; 8.24
$C_9H_{19}O_4P$.	Calculated %:	C 48.64; H 8.54

Dipropyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_3H_7\text{-}n)_2$. Reaction between 6 g of propyl alcohol, 7.9 g of dry pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 9 g (72%) of a substance having b.p. 113° (1 mm); d_4^{20} 1.0141; n_D^{20} 1.4439

	Found %:	C 52.61; 52.78; H 9.37; 9.42
$C_{11}H_{23}O_4P$.	Calculated %:	C 52.80; H 9.92

Diisopropyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 7 g of an ester having b.p. 99° (2 mm); d_4^{20} 0.9973; n_D^{20} 1.4360

	Found %:	P 12.43; 12.37
$C_{11}H_{23}O_4P$.	Calculated %:	P 12.40

Dibutyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_4H_9\text{-}n)_2$. To a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Two successive fractionations yielded 9.3 g of ester having b.p. 132-133° (2 mm); d_4^{20} 0.9910; n_D^{20} 1.4460

	Found %:	C 55.77; 55.71; H 9.86; 10.01
$C_{13}H_{27}O_4P$.	Calculated %:	C 56.11; H 9.71

Diisobutyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 7.4 g of isobutyl

alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 9 g of a substance having b.p. 116° (1 mm); d_4^{20} 0.9847; n_D^{20} 1.4440

	Found %:	C 56.21; 56.00; H 9.89; 9.86
$C_{13}H_{27}O_4P$.	Calculated %:	C 56.11; H 9.71

Diallyl 2-Isopropoxyvinylphosphonate i-C_3H_7OCH = $CHPO(OC_3H_5)_2$. To a mixture of 5.8 g of allyl alcohol and 8 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 8 g (54%) of a substance having b.p. 120° (2 mm); d_4^{20} 1.0448; n_D^{20} 1.4651

	Found %:	C 53.88; 54.02; H 8.10; 7.95
$C_{11}H_{19}O_4P$.	Calculated %:	C 53.65; H 7.72

Dihexyl 2-Isopropoxyvinylphosphonate i-C_3H_7OCH = $CHPO(OC_6H_{13}\text{-}n)_2$. To a mixture of 21 g of hexyl alcohol and 7.9 g of pyridine 10.15 g 2-isopropoxyvinylphosphonic dichloride was added. Fractionation yielded 8.5 g of a substance having b.p. 149° (2 mm); d_4^{20} 0.9628; n_D^{20} 1.4498

	Found %:	C 61.17; 61.13; H 10.58; 10.58
$C_{17}H_{35}O_4P$.	Calculated %:	C 61.07; H 10.47

Bis(2-methoxyethyl) 2-Isopropoxyvinylphosphonate i-C_3H_7OCH = $CHPO(OCH_2 - CH_2OCH_3)_2$. Reaction of a mixture of 7.6 g of 2-methoxyethanol, 7.9 g of pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 8 g (57%) of a substance having b.p. 155° (3 mm); d_4^{20} 1.1002; n_D^{20} 1.4555.

	Found %:	C 46.81; 46.91; H 8.11; 8.19
$C_{11}H_{23}O_6P$.	Calculated %:	C 46.80; H 8.15

Bis(2-ethoxyethyl) 2-Isopropoxyvinylphosphonate i-C_3H_7OCH = $CHPO(OCH_2 = CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 100 ml of benzene 10.15 g of 2-isopropoxyvinylphosphonic dichlonde was added. Fractionation yielded 5 g of ester, b.p. 155° (1 mm); d_4^{20} 1.0652; n_D^{20} 1.4520

	Found %:	C 49.98; 50.10; H 8.78; 8.98
$C_{13}H_{27}O_6P$.	Calculated %:	C 50.32; H 8.70

Diesters of 2-Isobutoxyvinylphosphonic Acid

Dimethyl 2-Isobutoxyvinylphosphonate i-C_4H_9OCH = $CHPO(OCH_3)_2$. A solution of 3.2 g of methyl alcohol and 7.9 g of pyridine in 75 ml of benzene was prepared, and 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 7.7 g (75%) of an ester having b.p. 105° (2 mm); d_4^{20} 1.0831; n_D^{20} 1.4487

	Found %:	C 46.24; 45.99; H 8.08; 8.09
$C_8H_{17}O_4P$.	Calculated %:	C 46.15; H 8.17

Methyl 2-isobutoxyvinylphosphonate is a colorless liquid, soluble in the usual organic solvents and in water.

Diethyl 2-Isobutoxyvinylphosphonate i-C_4H_9OCH = $CHPO(OC_2H_5)_2$. To a solution of 4.6 g of ethyl alcohol and 7.9 g of pyridine in 60 ml of benzene 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. At 110° (2 mm) 8.6 g (73%) of an ester came over; it had d_4^{20} 1.0310; n_D^{20} 1.4435

	Found %:	C 50.48; 50.26; H 8.67; 8.73
$C_{10}H_{21}O_4P$.	Calculated %:	C 50.84; H 8.89

Dipropyl 2-Isobutoxyvinylphosphonate i-C_4H_9OCH = $CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol, 7.9 g of pyridine, and 80 ml of benzene, 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product was 10.5 g of a substance having b.p. 124° (2 mm); d_4^{20} 1.0014; n_D^{20} 1.4442.

	Found %:	C 54.43; 54.45; H 9.34; 9.52
$C_{12}H_{25}O_4P$.	Calculated %:	C 54.54; H 9.46

Diisopropyl 2-Isobutoxyvinylphosphonate i-C_4H_9OCH = $CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol, 7.9 g of pyridine, and 80 ml of benzene, 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. Three successive vacuum distillations yielded 6.6 g of a substance having b.p. 110° (2 mm); d_4^{20} 0.9948; n_D^{20} 1.4405

	Found %:	C 54.62; 54.49; H 9.23; 9.31
$C_{12}H_{25}O_4P$.	Calculated %:	C 54.54; H 9.46

Dibutyl 2-Isobutoxyvinylphosphonate i-C_4H_9OCH = $CHPO(OC_4H_9\text{-}n)_2$. Reaction between 7.4 g of butyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-isobutoxyvinylphosphonic dichloride yielded 10.4 g (70%) of a substance

having b.p. 144° (1 mm); d_4^{20} 0.9849; n_D^{20} 1.4470

	Found %:	C 57.90; 57.92; H 10.32; 10.21
$C_{14}H_{29}O_4P$.	Calculated %:	C 57.53; H 9.93

Diisobutyl 2-Isobutoxyvinylphosphonate i-$C_4H_9OCH = CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 7.4 g of isobutyl alcohol and 7.9 g of pyridine 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 9.8 g of ester, b.p. 135° (2 mm); d_4^{20} 0.9804; n_D^{20} 1.4440

	Found %:	C 57.40; 57.32; H 9.97; 9.78
$C_{14}H_{29}O_4P$.	Calculated %:	C 57.53; H 9.93

Diallyl 2-Isobutoxyvinylphosphonate i-$C_4H_9OCH = CHPO(OCH_2 - CH = CH_2)_2$. To a mixture of 5.8 g of allyl alcohol, 7.9 g of pyridine, and 60 ml of benzene 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 9.5 g of ester, b.p. 130° (1 mm); d_4^{20} 1.0417; n_D^{20} 1.4643

	Found %:	C 55.58; 55.52; H 8.26; 8.08
$C_{12}H_{21}O_4P$.	Calculated %:	C 55.38; H 8.07

Dihexyl 2-Isobutoxyvinylphosphonate i-$C_4H_9OCH = CHPO(OC_6H_{13}\text{-}n)_2$. Reaction between 10.85 g of isobutoxyvinylphosphonic dichloride, 10.21 g of hexyl alcohol, and 7.9 g of pyridine yielded 10.5 g of a substance having b.p. 165° (1 mm); d_4^{20} 0.9597; n_D^{20} 1.4498

	Found %:	C 62.19; 61.97; H 10.84; 10.81
$C_{18}H_{37}O_4P$.	Calculated %:	C 62.06; H 10.63

Bis(2-methoxyethyl) 2-Isobutoxyvinylphosphonate i-$C_4H_9OCH = CHPO(OCH_2 - CH_2OCH_3)_2$. To a mixture of 7.6 g of 2-methoxyethanol and 7.9 g of pyridine 10.85 g of isobutoxyvinylphosphonic dichloride was added. The product was 10.4 g of a substance having b.p. 163° (2 mm); d_4^{20} 1.0900; n_D^{20} 1.4543

	Found %:	C 48.45; 48.69; H 8.36; 8.36
$C_{12}H_{25}O_6P$.	Calculated %:	C 48.64; H 8.44

Bis(2-ethoxyethyl) 2-Isobutoxyvinylphosphonate i-$C_4H_9OCH = CHPO(OCH_2 - CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 70 ml of benzene 10.85 g of isobutoxyvinylphosphonic dichloride was added. The product was 10.6 g of ester, b.p. 170° (2 mm); d_4^{20} 1.0533; n_D^{20} 1.4509

	Found %:	C 52.00; 51.88; H 8.87; 8.84
$C_{14}H_{29}O_6P$.	Calculated %:	C 51.85; H 8.95

Diesters of 2-Isopentyloxyvinylphosphonic Acid

Dimethyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH - CH_2 - CH_2 - OCH = CHPO(OCH_3)_2$. To a mixture of 3.2 g of methyl alcohol, 7.9 g of pyridine, and 50 ml of benzene 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 7 g of ester, b.p. 109.5° (1 mm); d_4^{20} 1.0667; n_D^{20} 1.4508

	Found %:	C 48.40; 48.54; H 8.72; 8.41
$C_9H_{19}O_4P$.	Calculated %:	C 48.64; H 8.55

Diethyl 2-Isopentyloxyvinylphsophonate $(CH_3)_2CH - CH_2 - CH_2OCH = CHPO(OC_2H_5)_2$. To a mixture of 4.6 g of ethyl alcohol and 7.9 g of pyridine 11.55 g of 2-pentyloxyvinylphosphonic dichloride was added. The product was 8 g of a substance having b.p. 119° (1 mm); d_4^{20} 1.0928; n_D^{20} 1.4464

	Found %:	C 52.65; 52.58; H 9.21; 9.28
$C_{11}H_{23}O_4P$.	Calculated %:	C 52.80; H 9.20

Dipropyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH - CH_2 - CH_2OCH = CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol, 7.9 g of pyridine, and 75 ml of benzene 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 8 g of a substance having b.p. 132° (1 mm); d_4^{20} 0.9960; n_D^{20} 1.4482

	Found %:	C 55.77; 55.68; H 9.73; 10.05
$C_{13}H_{27}O_4P$.	Calculated %:	C 56.11; H 9.71

Diisopropyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CHCH_2 - CH_2OCH = CHPO(OC_3H_7\text{-}i)_2$. Reaction between 6 g of isopropyl alcohol, 7.9 g of pyridine, and 11.55 g of 2-isopentyloxyvinylphosphonic dichloride yielded 6 g of ester, b.p. 120° (2 mm); d_4^{20} 0.9866; n_D^{20} 1.4418

	Found %:	C 55.97; 56.19; H 9.64; 9.79
$C_{13}H_{27}O_4P$.	Calculated %:	C 56.11; H 9.71

Dibutyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_4H_9\text{-}n)_2$. A solution of 11.55 g of 2-isopentyloxyvinylphosphonic dichloride in 15 ml of dry benzene was added to a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine. The product was 7 g of an ester, b.p. 148° (1 mm); d_4^{20} 0.9896; n_D^{20} 1.4490

	Found %:	P 10.15; 9.97
$C_{15}H_{31}O_4P$.	Calculated %:	P 10.13

Diisobutyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 6.4 g of isobutyl alcohol, 6.83 g of pyridine, and 60 ml of benzene 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. Two successive fractionations yielded 6.5 g of ester, b.p. 143° (2 mm); d_4^{20} 0.9734; n_D^{20} 1.4458

	Found %:	P 10.14; 10.14
$C_{15}H_{31}O_4P$.	Calculated %:	P 10.13

Diallyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_3H_5)_2$. Reaction between 5.2 g of allyl alcohol, 6.83 g of pyridine, and 10 g of 2-isopentyloxyvinylphosphonic dichloride yielded 6.7 g of a substance having b.p. 137° (1 mm); d_4^{20} 1.0335; n_D^{20} 1.4645

	Found %:	P 10.88; 11.11
$C_{13}H_{25}O_4P$.	Calculated %:	P 11.31

Dihexyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_6H_{13}\text{-}n)_2$. A solution of 10 g of 2-isopentyloxyvinylphosphonic dichloride in 15 ml of benzene was added to a mixture of 6.84 g of hexyl alcohol, 6.83 g of pyridine, and 75 ml of benzene. The product was 9.2 g of ester, b.p. 171° (1 mm); d_4^{20} 0.9618; n_D^{20} 1.4500

	Found %:	P 8.61; 8.33
$C_{19}H_{39}O_4P$.	Calculated %:	P 8.56

Bis(2-methoxyethyl) 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OCH_2-CH_2OCH_3)_2$. To a mixture of 6.5 g of 2-methoxyethanol and 6.83 g of pyridine 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. Three successive vacuum distillations yielded 5.5 g of ester, b.p. 173° (1 mm); d_4^{20} 1.0758; n_D^{20} 1.4550

	Found %:	P 9.80; 10.00
$C_{13}H_{27}O_6P$.	Calculated %:	P 10.00

Bis(2-ethoxyethyl) 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OCH_2-CH_2OC_2H_5)_2$ To a mixture of 7.78 g of 2-ethoxyethanol, 6.83 g of pyridine, and 50 ml of benzene 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 6 g of a substance having b.p. 179° (1 mm); d_4^{20} 1.0453; n_D^{20} 1.4527

	Found %:	C 53.22; 53.43;	H 9.03; 9.17
$C_{15}H_{31}O_6P$.	Calculated %:	C 53.25;	H 9.17

SUMMARY

The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids have been prepared by the action of alcohols on 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic dichlorides. The properties of the esters have been described.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 240.*

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy
of Sciences

* Consultant's Bureau Translation, p. 213.

BLANK
PAGE

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 7. DIESTERS OF 2-PHENOXYVINYLPHOSPHONIC ACID

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

In continuation of our previous investigations on the synthesis of esters of 2-alkoxyvinylphosphonic acids by the action of alcohols on 2-alkoxyvinylphosphonic dichlorides in presence of pyridine [1] we have prepared esters of 2-phenoxyvinylphosphonic acid by analogous means. The esters obtained are colorless viscous liquids that can be vacuum-distilled without decomposition. They are all soluble in organic solvents, but are insoluble in water.

Some constants of the 2-phenoxyvinylphosphonic esters obtained are given in the table.

TABLE

Formula of substance	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$C_6H_5-O-CH=CHPO(OCH_3)_2$	128 (2)	1.5233	1.2871
$C_6H_5-O-CH=CHPO(OC_2H_5)_2$	140 (2)	1.5070	1.1367
$C_6H_5-O-CH=CHPO(OC_3H_7\text{-}n)_2$	147 (2)	1.4994	1.0934
$C_6H_5-O-CH=CHPO(OC_3H_7\text{-}i)_2$	135 (2)	1.4970	1.0870
$C_6H_5-O-CH=CHPO(OC_4H_9\text{-}n)_2$	165 (2)	1.4971	1.0648
$C_6H_5-O-CH=CHPO(OC_4H_9\text{-}i)_2$	157 (2)	1.4938	1.0596
$C_6H_5-O-CH=CHPO(OC_5H_5)_2$	153 (2)	1.5220	1.1330
$C_6H_5-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	204 (1)	1.4925	1.0237
$C_6H_5-O-CH=CHPO(O-CH_2-CH_2-O-CH_3)_2$	188 (2)	1.5070	1.1755
$C_6H_5-O-CH=CHPO(O-CH_2-CH_2-O-C_2H_5)_2$	198 (2)	1.5014	1.1386

The boiling points, refractive indices, and densities of 2-phenoxyvinylphosphonic esters are higher than those of the corresponding esters of 2-n-alkoxyvinylphosphonic acids.

EXPERIMENTAL

Dimethyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OCH_3)_2$. A mixture of 3.2 g of methyl alcohol, 7.9 g of pyridine, and 50 ml of benzene was introduced into a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser protected by a calcium chloride tube. The mixture was stirred and cooled with ice and salt while a mixture of 11.85 g of 2-phenoxyvinylphosphonic dichloride and 15 ml of benzene was added. Pyridine hydrochloride was filtered off, and the filtrate was washed with sodium carbonate solution and dried with calcined sodium sulfate. The solvent was distilled from a water bath, and the residue was vacuum-fractionated. Refractionation yielded 8 g of ester, b.p. 128° (2 mm); d_4^{20} 1.2871; n_D^{20} 1.5233.

Found %: P 13.39; 13.41

$C_{10}H_{13}O_4P$. Calculated %: P 13.59

All the other esters were synthesized by this method.

Diethyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OC_2H_5)_2$. To a mixture of 4.6 g of ethyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 10 g of a substance having b.p. 140° (2 mm); d_4^{20} 1.1367; n_D^{20} 1.5070

Found %: C 56.39; 56.43; H 6.63; 6.76

$C_{12}H_{17}O_4P$. Calculated %: C 56.25; H 6.64

Dipropyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10 g of ester having b.p. 147° (2 mm); d_4^{20} 1.0934; n_D^{20} 1.4994

Found %: C 59.06; 58.91; H 7.65; 7.44

$C_{14}H_{21}O_4P$. Calculated %: C 59.15; H 7.39

Diisopropyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol, 7.9 g of pyridine, and 80 ml of benzene 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 6 g of a substance having b.p. 135° (2 mm); d_4^{20} 1.0870; n_D^{20} 1.4970.

Found %: C 59.10; 59.33; H 7.31; 7.21

$C_{14}H_{21}O_4P$. Calculated %: C 59.15; H 7.39

Dibutyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_4H_9\text{-}n)_2$. To a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Two successive fractionations yielded 10.7 g of ester, b.p. 165° (2 mm); d_4^{20} 1.0648; n_D^{20} 1.4971

Found %: P 9.75; 9.77

$C_{18}H_{29}O_4P$. Calculated %: P 9.93

Diisobutyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_4H_9\text{-}i)_2$. Reaction between 7.4 g of isobutyl alcohol, 7.9 g of pyridine, and 11.85 g of 2-phenoxyvinylphosphonic dichloride yielded 11 g of a substance having b.p. 157° (2 mm); d_4^{20} 1.0596; n_D^{20} 1.4938.

Found %: C 61.22; 61.21; H 7.90; 7.90

$C_{18}H_{29}O_4P$. Calculated %: C 61.53; H 8.01

Diallyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_3H_5)_2$. To a mixture of 5.8 g of allyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 5 g of ester, b.p. 153° (2 mm); d_4^{20} 1.1330; n_D^{20} 1.5220.

Found %: C 59.47; 59.60; H 6.15; 6.32

$C_{14}H_{17}O_4P$. Calculated %: C 60.00; H 6.07

Diallyl 2-phenoxyvinylphosphonate is a clear viscous liquid; it polymerizes when heated in presence of benzoyl peroxide.

Dihexyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_6H_{13}\text{-}n)_2$. To a mixture of 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 50 ml of benzene, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10.8 g of a substance having b.p. 204° (1 mm); d_4^{20} 1.0237; n_D^{20} 1.4925

Found %: C 65.15; 65.25; H 8.80; 8.81

$C_{18}H_{33}O_4P$. Calculated %: C 65.21; H 8.94

Bis(2-methoxyethyl) 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OCH_2-CH_2OCH_3)_2$. A mixture of 7.6 g of 2-methoxyethanol and 7.9 g of pyridine was diluted with 70 ml of benzene, and 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 11.2 g of ester, b.p. 188° (2mm); d_4^{20} 1.1755; n_D^{20} 1.5070

Found %: C 53.45; 53.27; H 6.48; 6.73

$C_{14}H_{21}O_6P$. Calculated %: C 53.16; H 6.64

Bis(2-ethoxyethyl) 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OCH_2-CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10 g of ester, b.p. 198° (2 mm); d_4^{20} 1.1386; n_D^{20} 1.5014

Found %: C 55.62; 55.64; H 7.30; 7.50

$C_{16}H_{25}O_5P$. Calculated %: C 55.81; H 7.26

SUMMARY

The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-phenoxyvinylphosphonic acid have been prepared by the action of 2-phenoxyvinylphosphonic dichloride on alcohols in presence of pyridine. The properties of these esters have been described.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955 No. 2, 240. *(See Consultant's Bureau Translation, p. 213.

Received June 11, 1954

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

ACTION OF SOME ALKOXY COMPOUNDS ON TRIALKOXY- AND DIALKOXYCHLORO-STIBINES

B. A. Arbuzov and O. D. Samoilova

Organoantimony compounds in which different alkoxy groups are attached to the same antimony atom are unknown. It appeared to us that the most promising method of synthesis of mixed alkoxystibines was the method of partial transesterification, since this method was the simplest and most convenient for antimonous esters [1]. The transesterification method, or alcoholysis, is applicable to carboxylic esters [2] and esters of some inorganic acids [3]. However, whereas the transesterification of esters of orthosilicic, orthotitanic, boric, and phosphorous acids requires the presence of an alkaline or acid catalyst, antimonous esters undergo transesterification when treated with alcohols in absence of catalyst.

The syntheses of mixed esters of antimonous acid were effected by partial transesterification of triethyl antimonite triethoxystibine with an equimolecular amount of a higher alcohol. For antimonous esters partial transesterification proceeds with simultaneous formation of three products, which result by the replacement of one, two, and three R radicals, respectively, by R', as indicated in the equation:

$$Sb(OR)_3 + R'OH \rightarrow \begin{cases} Sb(OR)_2(OR') + ROH \\ Sb(OR)(OR')_2 + 2ROH \\ Sb(OR')_3 + 3ROH \end{cases}$$

The unsymmetrical esters were separated in the first fractionation. It was found that the temperature of the oil bath must be carefully controlled, for redistillation and overheating cause disproportionation of the esters with formation of the symmetrical antimonous esters. Symmetrization occurs very readily when the mixed esters are heated for a short time; thus, when butoxydiethoxystibine was heated for the purpose of fractionation, triethyl and tributyl antimonites were isolated. The same phenomenon was observed in the course of the redistillation of ethoxybisisopentyloxystibine.

Butoxydiethoxy-, diethoxyisopentyloxy-, diethoxyhexyloxy-, dibutoxyethoxy-, ethoxybisisopentyloxy-, and ethoxybishexyloxy-stibines were prepared by the method of partial transesterification. These substances are colorless, fairly mobile liquids, which are very readily hydrolyzed when exposed to the atmosphere, so that it was difficult to measure their physical constants. The physical constants of the synthesized esters are given in the table.

Although the method of partial transesterification has been applied with success to the reaction of trialkyl and dialkyl hydrogen phosphites with higher alcohols, such as octyl, nonyl, and hexadecyl alcohols, we have not succeeded in preparing unsymmetrical antimonous esters having radicals higher than hexyl; only symmetrical esters were obtained.

TABLE

$Sb(OR)_n(OR')_{3-n}$	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$Sb(OC_2H_5)_2(OC_4H_9\text{-}n)$	109-110 (7)	1.4902	1.3990
$Sb(OC_2H_5)(OC_4H_9\text{-}n)_2$	129-130 (7)	1.4861	1.3051
$Sb(OC_2H_5)_2(OC_5H_{11}\text{-}i)$	120-121 (6)	1.4856	1.3452
$Sb(OC_2H_5)(OC_5H_{11}\text{-}i)_2$	136-137 (3)	1.4815	1.2630
$Sb(OC_2H_5)_2(OC_6H_{13})$	151-152 (4)	1.4840	1.3313
$Sb(OC_2H_5)(OC_6H_{13})_2$	171-172 (4)	1.4743	1.1982

The transesterification of antimonous esters occurs not only with alcohols, but also with other alkoxy compounds. We found that, when triethoxystibine was treated with carboxylic esters, exchange occurred very readily between the alkoxy radicals of the two esters (at the boiling point of the carboxylic ester, in absence of catalyst):

$$Sb(OC_2H_5)_3 + 3ROOCCH_2R' \rightarrow Sb(OR)_3 + 3R'CH_2COOC_2H_5.$$

We have studied the actions of butyl acetate, isopentyl acetate, and phenyl benzoate on triethoxystibine, and have obtained, respectively tributoxy-, trisisopentyloxy-, and triphenoxy-stibine. It should be noted that the higher the alkoxy radical of the carboxylic ester, the more complete the transesterification; transesterification by means of butyl acetate was found to be much more difficult than transesterification by means of isopentyl acetate.

The replacement of an alkoxy radical in an antimonous ester occurs also when the ester is treated with a carboxylic acid, when the corresponding alcohol is eliminated and a mixed anhydride of the carboxylic acid with

the diester of antimonous acid is formed. Thus, reaction of acetic acid with triethoxystibine led to the synthesis of acetoxydiethoxystibine. This compound is thermally unstable: it decomposes at 100-105° with formation of ethyl acetate.

The ability to undergo transesterification under mild conditions is not confined to trialkoxystibines. Our experiments show that dialkoxychlorostibines are also able to react with higher alcohols with replacement of alkoxy groups; the chlorine is not affected. By the action of two molecular proportions of butyl alcohol on chlorodiethoxystibine, of isopentyl alcohol on chlorodiethoxystibine, and of hexyl alcohol on dibutoxychlorostibine, we synthesized dibutoxychlorostibine, chlorobisisopentyloxystibine, and chlorobishexyloxystibine, respectively. The reactions went smoothly and gave almost quantitative yields of the dialkoxychlorostibines having the longer radical; they are suitable as preparative methods.

EXPERIMENTAL

Reaction of Triethoxystibine with Butyl Alcohol. Equimolecular amounts of triethoxystibine (18 g) and butyl alcohol (4.5 g) were placed in an Arbuzov flask. The reaction mixture was heated at 110-115°, and 2.8 g of ethyl alcohol came over at 78-84° (the theoretical amount was 3.2 g). Fractionation of the reaction products yielded:

Frac. I, b.p. 87 – 89° (7 mm); 6.4 g
Frac. II, b.p. 89 – 109(7 mm); 0.8 g
Frac. III, b.p. 109–110° (7 mm); 4.9 g
Frac. IV, b.p. 110–129° (7 mm); 0.5 g
Frac. V b.p. 129–130° (7 mm); 3.2g
Frac. VI b.p. 130–140° (7 mm); 0.4 g
Frac. VII b.p. 140 – 141° (7 mm); 1.3g

The boiling point of Fraction I indicated that it was unchanged triethoxystibine. Fraction III b.p. 109-110° (7 mm); d_4^{20} 1.3990; n_D^{20} 1.4902, was butoxydiethoxystibine, a liquid that was readily hydrolyzed by the moisture of the air.

Found %: Sb 42.91; 42.55
$C_8H_{19}O_3Sb$. Calculated %: Sb 42.72

Fraction V, b.p. 129-130° (7 mm); d_4^{20} 1.3051; n_D^{20} 1.4861, was dibutoxyethoxystibine.

Found %: Sb 39.30
$C_{10}H_{23}O_3Sb$. Calculated %: Sb 38.94

The boiling point of Fraction VII indicated that it was tributoxystibine.

Effect of High Temperature on Butoxydiethoxystibine. Butoxydiethoxystibine (4.9 g) was heated at 150-160° for 20 minutes in an Arbuzov flask. Fractionation of the reaction products yielded:

Frac. I, b.p. 82- 83° (5 mm); 2.9 g
Frac. II, b.p. 136-137° (5 mm); 1.6 g

The boiling point of Fraction I indicated that it was triethoxystibine. Fraction II (b.p. 136-137°/5 mm) was tributoxystibine.

Reaction of Triethoxystibine with Isopentyl Alcohol. A mixture of 20 g of triethoxystibine and 6.8 g of isopentyl alcohol (obtained from fusel oil and boiling at 131-132°) was heated at 120-125°. Ethyl alcohol (2.9 g, the theoretical amount being 3.6 g) came over at 78-72°. Fractionation of the reaction product yielded:

Frac. I, b.p. 84-85° (6 mm); 3.2g
Frac. II, b.p. 85-119°(6 mm); 0.6g
Frac. III, b.p. 119-120°(6 mm); 4.5g
Frac. IV, b.p. 120-132°(3 mm); 0.9g
Frac. V, b.p. 132-133° (3 mm); 4.9g
Frac. VI, b.p. 133-150° (3 mm); 0.4 g
Frac. VII, b.p. 151-152° (3 mm); 7.2g

The boiling points of Fractions I and VII indicated that these fractions were triethoxy- and trisisopentyloxy-stibine, respectively. Fraction III, b.p. 120-121° (6 mm); d_4^{20} 1.3452; n_D^{20} 1.4856, was diethoxyisopentyloxystibine.

Found %: Sb 41.13; 41.17

$C_9H_{21}O_3Sb$. Calculated %: Sb 40.75

Fraction V, b.p. 136-137° (3 mm); d_4^{20} 1.2630; n_D^{20} 1.4815, was ethoxybisisopentyloxystibine.

Found %: Sb 35.77; 35.70

$C_{12}H_{27}O_3Sb$. Calculated %: Sb 35.73

Redistillation of Ethoxybisisopentyloxystibine. Vacuum distillation of 4.5 g of ethoxybisisopentyloxystibine from an Arbuzov flask yielded:

Frac. I, b.p. 84-85° (6 mm); 1.0g
Frac. II, b.p. 157-158° (6 mm); 2.7g.

The boiling points of the fractions indicated that the first was triethoxystibine and the second trisisopentyloxystibine.

Reaction of Triethoxystibine with Hexyl Alcohol. Equimolecular amounts of triethoxystibine (18 g) and hexyl alcohol (7.1 g) were heated together in an Arbuzov flask at 120-125°. Ethyl alcohol came over at 78-85° (2.0 g, the theoretical amount being 2.8 g). Fractionation of the reaction products yielded:

Frac. I, b.p. 85-105° (8 mm); 6.2g
Frac. II, b.p. 133-135° (4 mm); 2.3g
Frac. III, b.p. 135-170° (4 mm); 0.7g
Frac. IV, b.p. 170-173° (4 mm); 2.1g
Frac. V, b.p. 190-191° (4 mm); 4.6g

Fraction I was redistilled and boiled at 94-95° (10 mm), which corresponded to triethoxystibine. Fraction VI was trishexyloxystibine. Fraction II, b.p. 133-135° (4 mm); n_D^{20} 1.4840; d_4^{20} 1.3313, was diethoxyhexyloxystibine.

Found %: Sb 39.89; 39.12

$C_{16}H_{33}O_4Sb$. Calculated %: Sb 38.93

Fraction IV, b.p. 170-173° (4 mm); n_D^{20} 1.4743; d_4^{20} 1.1982, was ethoxybishexyloxystibine.

Found %: Sb 33.53; 33.39

$C_{14}H_{31}O_3Sb$. Calculated %: Sb 33.02

Reaction of Triethoxystibine with Butyl Acetate. A mixture of 4 g of triethoxystibine and 6 g of butyl acetate (b.p. 125-125.5°) was prepared in an Arbuzov flask. The mixture was heated at 100-110° for one hour, and a liquid very slowly distilled over (1 g; b.p. 77-85°); it was probably ethyl acetate. Fractionation of the reaction products yielded:

Frac. I, b.p. 124-126°; 3.2g
Frac. II, b.p. 95-96° (11 mm); 2.8 g
Frac. III, b.p. 139-141 (11 mm); 0.6 g

Fractions I and II were unchanged butyl acetate and unchanged triethoxystibine, respectively. The boiling point of Fraction III indicated that it was tributoxystibine.

Reaction of Triethoxystibine with Isopentyl Acetate. To 5 g of triethoxystibine 8 g of isopentyl acetate (b.p. 148-148.5°) was added. The mixture was heated at 110-115° for 45 minutes, and 4.8 g of a liquid came over at 78-87°. This liquid, which after redistillation had b.p. 78-79°; d_4^{20} 0.8906; n_D^{20} 1.3710, was ethyl acetate (the reported constants are b.p. 77.18°, d_4^{20} 0.92446 [4]. Fractionation of the reaction products yielded:

Frac. I b.p. 125-126°; 0.6 g
Frac. II b.p. 156-157° (6 mm); d_4^{20} 1.1885; 6.1g

The boiling point of Fraction II indicated that this fraction was trisisopentyloxystibine. It was obtained in 82.4 % yield.

Reaction of Triethoxystibine with Phenyl Benzoate. A mixture of 8 g of triethoxystibine and 18.6 g of phenyl benzoate was heated at 140-150° for 30 minutes. Fractionation of the reaction products yielded:

Frac. I b.p. 89-89.5° (10 mm); 12.8g
Frac. II, b.p. 238-242° (4 mm); 9.3 g

Fraction I, b.p. 89-89.5° (10 mm); d_4^{20} 1.0489; n_D^{20} 1.5064, was ethyl benzoate (the literature [5] gives b.p. 211.2°; d_4^{15} 1.0509; n_D^{15} 1.5079 [5]. The fraction boiling at 238-242° (4 mm) melted at 99-101°; it was difficult to

distill. It was triphenoxystibine and was obtained in 77.4 % yield.

Found %: Sb 30.09; 30.30

$C_{18}H_{15}O_3Sb$. Calculated %: Sb 30.38

Reaction of Triethoxystibine with Glacial Acetic Acid. Glacial acetic acid (2.3 g) was added slowly to 10 g of triethoxystibine. Reaction proceeded with evolution of heat. After the whole of the glacial acetic acid had been added the reaction mixture crystallized; there was no odor of ethyl acetate. The mixture was warmed in a water bath (60-65°), and at a residual pressure of 90 mm 1.4 g of a liquid came over at 35-40°; after being redistilled it had b.p. 78-78.5; d_4^{20} 0.7916. According to its physical constants the liquid was ethyl alcohol, for which the literature [6] gives b.p. 78.3°, d_4^{20} 0.78945. The residue in the flask crystallized out. A small amount of this residue was quickly washed with ether on a sintered-glass filter and then dried in a vacuum desiccator. It melted at 50-51°.

Found %: CH_3COOH 21.68

$C_6H_{13}O_4Sb$ Calculated %: CH_3COOH 22.15

Found %: Sb 44.72

$C_6H_{13}O_4Sb$ Calculated %: Sb 44.96

The crystalline product (9 g) was heated, and when the temperature of the oil bath was 100-110° the substance decomposed with separation of a liquid (2.1 g), and a white powder remained in the flask. The liquid was distilled twice and then had b.p. 77-78°; d_4^{20} 0.8931. According to its physical constants this liquid was ethyl acetate, for which the literature [4] gives b.p. 77.18° and d_4^{20} 0.92446 [4].

Action of Butyl Alcohol on Chlorodiethoxystibine. A mixture of 12 g of chlorodiethoxystibine (b.p. 106°/10 mm) and 6.8 g of butyl alcohol was prepared in an Arbuzov flask and was then heated at 110-115°, when ethyl alcohol came over at 77-82° (3.9 g). A Beilstein test for chlorine was negative. Vacuum distillation gave 14.6 g (90.0%) of a fraction having b.p. 147-148° (10 mm); d_4^{20} 1.5066. According to its physical constants the compound was dibutoxychlorostibine [7].

Action of Isopentyl Alcohol on Chlorodiethoxystibine. A mixture of 10 g of chlorodiethoxystibine and 6.3 g of isopentyl alcohol was heated at 110-115°, and 3.1 g of ethyl alcohol came over at 77-82°. A Beilstein test for chlorine was negative. Vacuum distillation gave 12.0 g (89.5%) of a fraction having b.p. 140-141° (3 mm); d_4^{20} 1.3691. The substance was chlorobisisopentyloxystibine.

Found %: Sb 37.10; 37.11; Cl 10.62; 10.41

$C_{10}H_{22}O_2ClSb$. Calculated %: Sb 36.76; Cl 10.70

Action of Hexyl Alcohol on Dibutoxychlorostibine. A mixture of 13 g of dibutoxychlorostibine was heated with 8.7 g of hexyl alcohol, and butyl alcohol distilled over at a residual pressure of 90 mm. The butyl alcohol (5.5 g) was redistilled and then boiled at 115–117°. The residue was vacuum-distilled and yielded 12.1 g (79.1%) of a fraction boiling at 170–172° (3 mm). The boiling point of the fraction indicated it to be chlorobishexyloxystibine [7].

SUMMARY

1. Both full and partial esters of antimonous acid are able to undergo transesterification when treated with alcohols or carboxylic esters.

2. Carboxylic acids react with antimonous esters with formation of mixed anhydrides.

3. Eight antimonous esters that have not been described previously were synthesized.

4. Dialkoxychlorostibines can undergo transesterification with higher alcohols with formation of dialkoxychlorostibines containing higher alkyl radicals.

LITERATURE CITED

[1] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951 No. 5, 551.

[2] C. Friedel and R. Crafts, Ann. 133, 207 (1865).

[3] B. A. Arbuzov and T. G. Shavsha, Proc. Acad. Sci. USSR, 68, 259 (1949); B. A. Arbuzov and Z. G. Isaeva, J. Gen. Chem. 22, 566 (1952)*; A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina, Bull. Acad. Sci.

* Consultant's Bureau Translation, p 629 .

[4] S. Young, E. Ferter, J. Chem. Soc. 83, 47 (1903)

[5] E. Linnemann, Ann. 160, 208 (1871); I. S. Lumsden, J. Chem. Soc. 87, 94 (1905).

[6] I. W. Winkler, Ber. 38, 3615, 1905; D. I. Mendeleev, Ann. Physik, 138, 103 (1869).

[7] B. A. Arbuzov and O. D. Samoilova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 6, 717.

Received July 9, 1954

A. M. Butlerov Research Institute
V. I. Ulyanov-Lenin State University
Kazan

BLANK
PAGE

SYNTHESIS OF CHLORAMPHENICOL

G. Fodor, J. Toth, E. Kovacs, and J. Kiss

Among the numerous methods that have been developed for the synthesis of 2-amino-1-phenyl-1-propanol (norephedrine) and its derivatives containing substituents in the benzene ring, the most widely applied is that of Bruckner and his coworkers [1, 2], in which the starting material is an (alkoxypropeny')benzene. Working by this method under Bruckner's direction, in 1943 I. Kovacs [3] prepared cinnamyl acetate (I), and she also prepared the acetic ester of 2-nitro-3-nitroso-3-phenyl-1-propanol (II), and from this, by treatment with acetic anhydride and sulfuric acid, the diacetic ester of 2-nitro-1-phenyl-1,3-propanediol (III). Electrolytic reduction of the last compound yielded 2-amino-1-phenyl-1,3-propanediol (IV) in the form of an N,O-diacetyl derivative.

The syntheses of compounds having structures similar to that of (IV) from halohydrins of cinnamyl alcohol had at that time been already reported in the literature [4, 5]. It was later shown, however, that these compounds were identical with 3-amino-3-phenyl-1,2-propanediol, a structural isomer of (IV) [6, 7].

Thus, the first synthesis of the compound (IV) was carried out at Szeged University. Later, this work acquired great importance, for the compound (IV) became one of the main intermediates in the synthesis of Chloromycetin (chloramphenicol) - an important antibiotic [6, 8].

In previous stereochemical investigations we have studied, in particular, the configuration of 2-amino-1-phenyl-1-propanol (norephedrine), including the spatial disposition (conformation) of the hydroxyl and amino groups [9].

In 1949 we extended our investigations to chloramphenicol (VIIIa). The investigations took two directions: a study of the stereochemistry of this compound [10], and attempts to synthesize it.

We succeeded in converting DL-chloramphenicol into DL-N-benzoylnorpseudoephedrine without touching the asymmetric carbon atoms, and so proved its threo configuration, since Freudenberg and coworkers had shown that the configuration at the C atom carrying the amino group in (+)-pseudoephedrine is analogous to the configuration of L-(+)-alanine [11]. On the other hand, the configuration at the C atom carrying the hydroxyl group in (+)-pseudoephedrine is analogous to the configuration of mandelic acid [12], which was recently solved, successfully and finally, when the correlation between the configurations of (+)-mandelic and L-(+)-lactic acids was established [13]. Also, Vogler, who refers to the conversion of 3-phenylserine into (IV) [14], has proved the threo configuration of 3-phenylserine [15]. Diacetyl derivatives of the nitro compound (IX) and also diacetyl derivatives of the compound (IV) were found to behave like pseudoephedrine in the N to O acyl migration process, which indicates that the hydroxyl and amino groups in these compounds are sterically close [10]. Dunitz [16] has given an X-ray diffraction diagram for bromamphenicol, and this, according to Preobrazhensky [17], also proves the conformation referred to above. In our further discussion we therefore use projection formulas [10, 17], and these show not only the threo configuration of these compounds, but also the actual structures of their molecules.

Our investigations were carried out on optically inactive compounds, and in the further discussion each projection formula must be envisaged together with its mirror image.

The present paper gives an account of the synthetic investigations that we began in 1949. Our object was to repeat the preparation of the diacetyl derivative of (IV), as described in the above-mentioned paper by I. Kovacs [3], improve it from the preparative point of view, verify the stereochemical processes occurring, and, most important of all, investigate the conversion of the compound (IV) into chloramphenicol.

Compounds (II) and (IIIa) were obtained in high yield and in a sufficiently pure state [3]. Treatment of (II) with bis(dichloroacetic) anhydride yielded O^3-acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). Hydrolysis of (IIIa) with weak acids yielded the crystalline nitro diol (IIIc), which, in the form of the sodium salt of its aci form, has been described by Rebstock and coworkers [6]. Both (IIIa) and (IIIb) were reduced electrolytically in a strongly acid medium. The reduction of (IIIb), however, was accompanied by hydrogenolysis of the chlorine atoms of the dichloroacetyl group with formation of a diacetyl derivative of (IV), identical with that obtained by the reduction of (IIIa). It should be noted that for both compounds the yield in the reduction reaction is low, but we have succeeded in effecting satisfactory catalytic reduction of (IIIa) over palladium, both

* These Hungarian authors' names have been given their native spellings, as they are known in British and American journals. If transcribed from the Russian, they would be G. Fodor, I. Tot, E. Kovach, and I. Kish. Publisher.

at normal and at high pressures.

The diacetyl derivative of (IV) was found to be identical with the compound obtained from the reduction product of DL-threo-3-phenylserine, indicating that this substance, and therefore also the nitro diacetic ester (IIIa), has the same configuration. Taking into account the fact that the crystalline cinnamyl acetate (I) is the trans form [18b], like the stable forms of some natural ethers derived from propenylbenzene [18a], we may conclude that the exchange NO $\rightleftharpoons$ $OCOCH_3$ is probably succeeded by a Walden inversion and that NO and NO_2 react at the double bond as in trans addition reactions. The mechanism of this process has not yet been investigated from the stereochemical point of view, but it is a fact that Bruckner's synthesis [1,2] leads to compounds of the threo-pseudoephedrine series [9b].

By the reductions of the aci form of the nitro compound (IIIc), Controulis and coworkers have prepared both threo and erythro racemates of (IV). This is understandable, since the liberation of the nitro diol from its salt can, with equal probability, yield either epimeric modification. However, in the course of the reduction of the crystalline stereochemical individual (IIIa), no such change can occur.

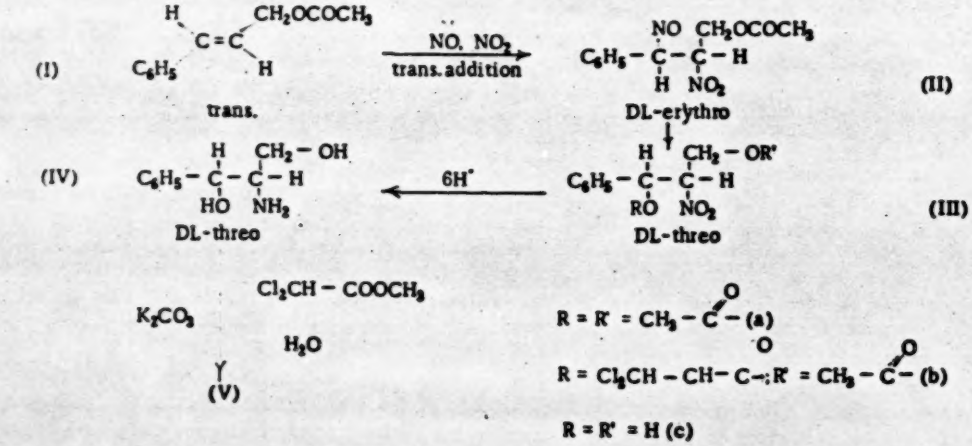
The conversion of the DL-threo amino diol (IV) into chloramphenicol had been effected prior to our work [6] as follows.

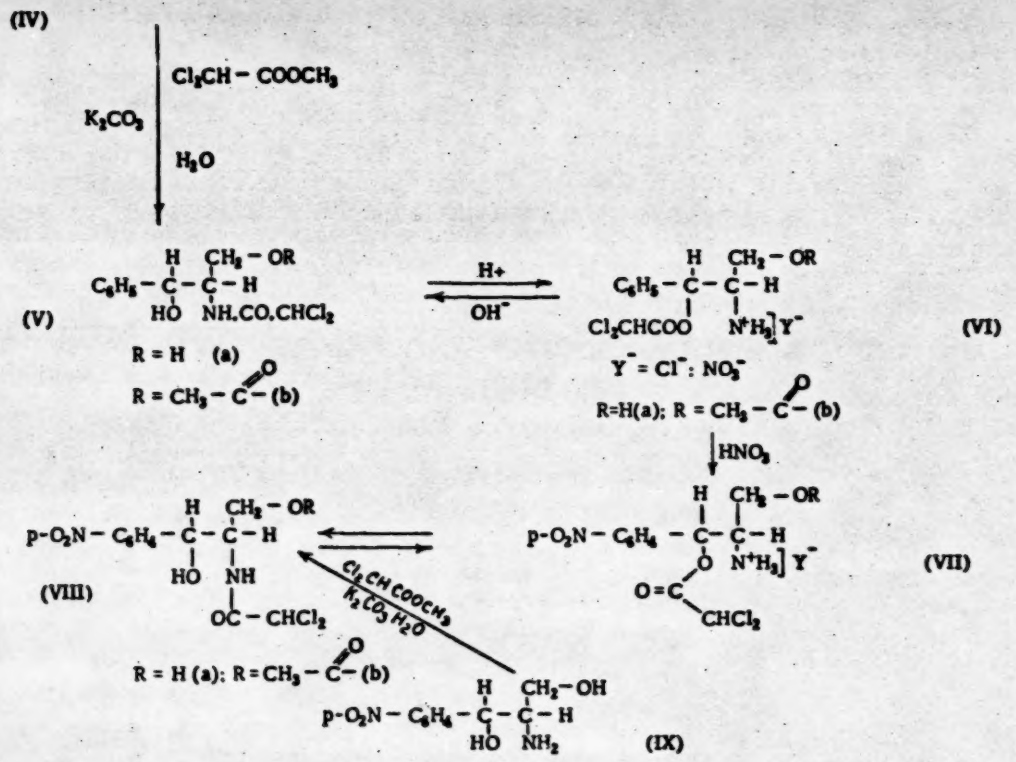
The triacetyl derivative of (IV) was nitrated, and the triacetyl derivative of (IX), which resulted, was deacetylated. A dichloroacetic acid residue was then introduced into the nitro amino diol (IX). We have found that the compound (IV) can be acylated, even in dilute aqueous solution, with methyl dichloroacetate, and we have isolated the previously undescribed DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va) in a crystalline state. It was found that this compound could be readily acylated on the primary hydroxyl group and that the resulting acetyl derivative (Vb) underwent a migration reaction in presence of acids, the acyl group then moving from the amino group to the secondary hydroxyl group.

In an alkaline medium this process proceeds in the reverse direction. During nitration, therefore, the two hydroxyl groups were protected with acyl groups, the amino group being protected by salt formation. The salt (VIIb) resulting from the nitration was converted by treatment with potassium carbonate into the O-acetylchloramphenicol (VIIIb), formed as a result of O to N acyl migration. When (VIIIb) was treated with caustic soda solution, it was converted immediately into (VIIIa), identical with DL-chloramphenicol. Nitration of the diacetic ester of (Va) (prepared by the complete acetylation of (Va)), followed by deacetylation of the resulting diacetyl derivative of (VIIIa), yielded the same final product.

As far as we know, the acylation of amines of this type with the aid of carboxylic esters in aqueous alkaline solution has not been described previously. In order to verify the general applicability of this method, we have acetylated (IV) with the aid of ethyl acetate, and we have also dichloroacetylated DL-2-amino-3-chloro-3-phenyl-1-propanol with the aid of methyl dichloroacetate.

The intermediate N-acyl (mainly dichloroacetyl) compounds were purified in the form of the readily crystallizing salts of their O-acyl isomers, which were prepared by N to O migration. After the purification, the acyl residue was again transferred to the amino group by the action of alkali.





Thus, on the basis of a stereochemical study of chloramphenicol, and also of a study of N to O acyl migration in compounds of similar type, we have succeeded in effecting its synthesis in a simple, stereochemically elucidated sequence: (I) ⟶ (II) ⟶ (III) ⟶ diacetyl derivative of (IV) ⟶ (Va) ⟶ (Vb) ⟶ (VIb) ⟶ ⟶ (VII) ⟶ (VIIIa)

EXPERIMENTAL

Cinnamyl Acetate (I). This acetic ester was prepared by the method of Cherbuliez and coworkers [4] by the action of acetic anhydride on cinnamyl alcohol in presence of sodium acetate. At the end of the reaction the excess of acetic anhydride was distilled off under reduced pressure; with this modification cinnamyl acetate was obtained in 95% yield; b.p. 117° (2 mm).

DL-eruthro-2-Nitro-3-nitroso-3-phenyl-1-propanol Acetic Ester (II). A mixture of 400 g of sodium nitrite and 250 ml of water was stirred in a jar of dark glass, and a solution of 90 g of cinnamyl acetate in 450 ml of toluene was added. Then, at 0° over a period of seven hours, 1400 ml of 20% sulfuric acid was added dropwise, carbon dioxide being occasionally passed through the mixture to stop foaming. When addition of sulfuric acid was complete, the precipitate present in the toluene layer was filtered off and washed with cold water. The crystalline mass that separated on the filter was rubbed out with 100 ml of ethanol, drained, and washed again with 50 ml of ethanol and 100 ml of ether free from peroxides. The product was 89 g (69%) of white DL-erythro-2-nitro-3-nitroso-3-phenyl-1-propanol acetic ester (II), m.p. 124°. I. Kovacs [3] gave m.p. 117°. After standing for some weeks the substance became colored as a result of decomposition.

Found %: C 52.66; H 4.96; N 10.85

$C_{11}H_{12}O_5N_2$. Calculated %: C 52.38; H 4.80; N 11.11

DL-threo-2-Nitro-1-phenyl-1,3-propanediol Diacetic Ester (IIIa). The nitroso nitro compound (II) (56 g) was mixed with 224 g of acetic anhydride and, at 25-29° with rapid agitation in a stream of carbon dioxide, a mixture of 24 g of concentrated sulfuric acid and 72 ml of acetic anhydride was added dropwise over a period of 40 minutes. Further stirring in a stream of carbon dioxide resulted in the formation of a light-yellow solution after about 50 minutes. The solution was filtered and poured into 1000 ml of ice water; stirring was continued for three hours. After the mixture had stood in a cold place for 3-4 days, the oil that separated crystallized. It was filtered off and dried; the yield was 43 g (69%). Recrystallization from ethanol or 75% acetic acid yielded

DL-threo-2-nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa), m.p. 72°. I. Kovacs [3] obtained a higher melting point; it is not clear why.

Found %: C 55.40; H 5.22; N 5.12
$C_{13}H_{15}O_8N$. Calculated %: C 55.51; H 5.38; N 4.98

DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). A mixture of 29 g of DL-erythro-2-nitro-3-nitroso-3-phenyl-1-propanol acetic ester (II) and 135 g of bis(dichloroacetic) anhydride was agitated vigorously in a stream of nitrogen, and a solution of 11.55 g of concentrated sulfuric acid in 24 g of bis-(dichloroacetic) anhydride was added dropwise at 25-29° over a period of 40 minutes. A reddish solution was obtained. Passage of nitrogen was continued for two hours, and the reaction mixture was then poured into 885 ml of water containing 11.9 g of sodium bicarbonate. Crystalline sodium acetate (184 g) was added, and the mixture was left for some days in a cold place. Most of the product, which separated in the form of an oil, solidified. The crystals were filtered off, washed with three 16-ml portions of 75% acetic acid, and vacuum-dried at 60°. The product was 18.4 g (46%) of crude DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb), m.p. 74°. Two recrystallizations from ethanol raised the melting point to 82°.

Found %: C 44.65; H 3.58; N 4.20; Cl 20.35
$C_{13}H_{13}O_8NCl_2$. Calculated %: C 44.46; H 3.74; N 4.00; Cl 20.25

DL-threo-2-Nitro-1-phenyl-1,3-propanediol (IIIc). Over a period of ten minutes 1156 ml of N HCl was added in portions to a solution of 54 g of 2-nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa) in 960 ml of acetone. The mixture was boiled for 3 hours 30 minutes, and was then evaporated down under reduced pressure to 600 ml and neutralized with 130 g of sodium bicarbonate. The resulting solution was extracted with ether. The ether layer was shaken with a solution of 30 g of potassium metabisulfite in 140 ml of water, dried with anhydrous magnesium sulfate, and evaporated to low bulk. When dry petroleum ether was added an oil separated, and this turned into a white powder when rubbed out. The product was 27 g (68.5%) of pure DL-threo-2-nitro-1-phenyl-1,3-propanediol (IIIc), m.p. 82.5°. Rebstock and coworkers [6] describe only the sodium salt of the aci form and do not cite analytical figures.

Found %: C 54.52; H 5.96; N 7.02
$C_9H_{11}O_4N$. Calculated %: C 54.82; H 5.62; N 7.10

DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol. 2-Nitro-1-phenyl-1,3-propanediol diacetic ester (28 g) was dissolved in 8 ml of glacial acetic acid and hydrogenated in presence of 5 g of palladium supported on bone charcoal (Pd content about 12%) at a pressure of 40 atm. After three hours the catalyst was filtered off and the solution was evaporated down at low temperature and under reduced pressure. The residue was recrystallized from 50 ml of anhydrous ethyl acetate. The product was 10 g (40%) of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol, m.p. 168-169°. I. Kovacs gives m.p. 158°. U. S. Patent 2483885 (Example 68) gives m.p. 167-168°.

Found %: C 62.03; H 6.75; N 5.46
$C_{13}H_{17}O_4N$. Calculated %: C 62.14; H 6.82; N 5.57

DL-threo-2-Acetamido-1-phenyl-1,3-propanediol Diacetic Ester. DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol (1 g) was stirred with 5 ml of quinoline, and 1.5 g of acetic anhydride was added. The reaction mixture was set aside for 24 hours and then evaporated down under reduced pressure. The oily residue was crystallized from methanol, and yielded 1.1 g (90%) of pure DL-threo-2-acetamido-1-phenyl-1,3-propanediol diacetic ester, m.p. 79-80°. U. S. Patent 2483885 (Example 68) gives m.p. 79°.

DL-threo-2-Amino-1-phenyl-1,3-propanediol (IV). a) DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol (25.12 g, i.e. 0.1 mole) was boiled with 5% hydrochloric acid for two hours, and the mixture was then evaporated to dryness under reduced pressure. The residue was crystallized from a 1 : 1 mixture of absolute ethanol and absolute ether, and yielded 16.8 g (82%) of the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol, m.p. 192°. It is evident that the substance of m.p. 178° described in U. S. Patent 2513346, Example 2d, was insufficiently pure.

Found %: C 53.24; H 6.85; N 6.64; Cl 17.50
$C_9H_{14}O_2NCl$. Calculated %: C 53.07, H 6.93; N 6.88; Cl 17.41

b) DL-threo-2-Nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa) (12.2 g), in 135 ml of anhydrous acetic acid containing 2.75 g of anhydrous oxalic acid, was hydrogenated at atmospheric pressure in presence of 2.5 g of palladium supported on bone charcoal (Pd content about 12%). When 3300 ml of hydrogen had been absorbed, the catalyst was filtered off and the solution was evaporated to dryness under reduced pressure. The residue

was extracted with 50 ml of ethanol, and the extract, after being filtered, was evaporated to dryness. The residue was dissolved in 30 ml of absolute ethanol containing 2.75 g of anhydrous oxalic acid, and the solution was set aside to crystallize. After one day the crystals that had separated were filtered off. They consisted of 6.4 g (59.5%) of the acid oxalate of DL-threo-2-amino-1-phenyl-1,3-propanediol, m.p. 139-140°.

	Found %:	C 51.22; H 5.98; N 5.64
$C_{11}H_{15}O_6N$.	Calculated %:	C 51.36; H 5.88; N 5.45

2-Amino-1-phenyl-1,3-propanediol (IV) was isolated from the acid oxalate in the usual way: yield 85%; m.p. 82-83°.

c) A solution of 10.2 g (0.05 mole) of the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol in 100 ml of water was rendered alkaline with 40% caustic soda solution (to pH 10). The solution was extracted with six 50-ml portions of ethyl acetate. The extract was dried with anhydrous sodium sulfate and evaporated down. The resulting oily product was crystallized from ethyl acetate, and yielded 5.85 g (70%) of DL-threo-2-amino-1-phenyl-1,3-propanediol (IV), m.p. 82-83°. U. S. Patent 2514376, Example 27, gives m.p. 81-83°.

	Found %:	C 64.64; H 7.75; N 8.21
$C_9H_{12}O_2N$.	Calculated %:	C 64.65; H 7.84; N 8.38

After standing, the mother liquor yielded 1.1 g of a white crystalline substance melting at 135°. The melting point and analytic results indicated that this compound was DL-threo-2-acetamido-1-phenyl-1,3-propanediol.

	Found %:	C 63.38; H 6.94; N 6.96
$C_{11}H_{15}O_3N$.	Calculated %:	C 63.14; H 7.23; N 6.70

Hydrolysis of this substance by the above-described method yielded the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol.

Preparation of DL-threo-2-Acetamido-1-phenyl-1,3-propanediol Diacetic Ester by Electrochemical Reduction. A solution was prepared by warming 14 g of DL-threo-2-nitro-1-phenyl-1,3-propanediol diacetic ester (recrystallized from 60% acetic acid) with a mixture of 100 ml of glacial acetic acid and 200 ml of 96% ethanol. The solution was cooled to room temperature and poured into a one-liter beaker containing mercury to the depth of 1 cm. The mercury had been given a preliminary wash with nitric acid. A 20% solution of nitric acid was used as anode liquor. The anode liquor was contained in a porous cylinder fixed in the beaker, and it was necessary that its level should be the same as that of the solution of the substance to be reduced. The cathode liquor was acidified with 8 ml of fuming hydrochloric acid, and reduction was effected at a current density of 0.07 amp/sq. cm at 44-45°. The desired temperature was maintained by ice cooling. After two hours the yellow color of the reaction mixture disappeared, and the end of the reaction (about three hours) was indicated by a vigorous evolution of hydrogen. The reaction mixture was neutralized with sodium acetate and was evaporated at 35-40° under reduced pressure to a volume of 80-100 ml. Solid sodium bicarbonate was added to the residue with constant stirring until evolution of carbon dioxide ceased.

The mixture was extracted with three 100-ml portions of chloroform, and the extract was dried with sodium sulfate and evaporated under reduced pressure until it attained the consistency of a sirup. The red oil so obtained was dissolved in acetic acid, treated with bone charcoal, and set aside for 24 hours in a refrigerator. The white crystalline powder that separated was filtered off and washed on the filter with 3 ml of ice-cooled ethyl acetate. The yield of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol [a diacetyl derivative of the compound (IV)] was 2.4 g. It melted at 162-164°, and after two recrystallizations from ethyl acetate its melting point was raised to 169-170°.

Electrochemical Reduction of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). The reduction was carried out in the apparatus described in the account of the preceding experiment. DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (3.5 g) was suspended in 40 ml of alcohol, and 2.5 ml of hydrochloric acid was added. Reduction was effected at a current density of 0.07 amp/sq. cm at 35-37°. The charge passed through the system was about 2.5 times the theoretical value. After the reduction treatment the mixture was stirred while 5 g of sodium bicarbonate was added. The reaction mixture was filtered and dried over sodium sulfate. The solution was evaporated to dryness under reduced pressure, and the resulting crystalline mass was extracted with hot ethyl acetate. The extract was evaporated under reduced pressure, and the crystalline substance obtained was recrystallized from ethyl acetate. The product was 0.7 g (28%) of a substance melting at 168°. A qualitative test for chlorine was negative.

	Found %:	C 61.90; H 6.87
$C_{13}H_{17}O_4$.	Calculated %:	C 62.14; H 6.82

Acylation of DL-threo-2-Amino-1-phenyl-1,3-propanediol with Esters in Aqueous Alkaline Medium.

a) Ethyl acetate (200 ml) was added to a solution of 16.7 g (0.1 mole) of 2-amino-1-phenyl-1,3-propanediol (IV) in 100 ml of water. The solution was stirred vigorously, and 30 ml of a 40% caustic soda solution was added dropwise at 30° over a period of 50 minutes, care being taken that the pH of the solution remained in the range 8-9. The water phase was separated and extracted five times with 50-ml portions of ethyl acetate. The combined ethyl acetate solution was dried over anhydrous sodium sulfate, filtered, and evaporated down. The glassy residue was dissolved in 50 ml of absolute ethanol, the solution was cooled with ice, and a two-fold excess of a solution of HCl in absolute ethanol was added. The crystals that came down were filtered off and washed with a small amount of absolute ethanol. The product was 12.4 g (50.5%) of the hydrochloride of DL-threo-O^3-acetyl-2-amino-1-phenyl-1,3-propanediol, m.p. 178°.

The salt so obtained (12.4 g) was dissolved in 40 ml of water, and 6.0 g of anhydrous potassium carbonate was added at 20°. After ten minutes the mixture was extracted ten times with 50-ml portions of ethyl acetate. Treatment of the extract yielded an oil, which was crystallized from ethyl acetate and yielded 8.5 g (41%) of pure DL-threo-2-acetamido-1-phenyl-1,3-propanediol, m.p. 136-138°. The substance showed no melting point depression in admixture with a sample prepared by another method [6, 8].

b) Methyl dichloroacetate (71.5 g, i.e. 0.5 mole) was added to a solution of 20.4 g (0.1 mole) of the hydrochloride of 2-amino-1-phenyl-1,3-propanediol (IV). The mixture was stirred vigorously for about one hour, and at 6-8° 30 ml (0.3 mole) of 40% caustic soda solution was added dropwise in such a way that the pH of the solution remained in the range 6-8 throughout the reaction. The aqueous phase was separated and extracted six times with 50-ml portions of ethyl acetate. The combined extract was dried over anhydrous sodium sulfate and filtered. The solvents were removed, and the oil remaining was dissolved in 50 ml of absolute ethanol. A solution of 30 ml (0.3 mole) of HCl in absolute ethanol was then added. The crystals that separated (m.p. 190°) were filtered off and washed with 200 ml of a 1 : 1 ethanol-ether mixture. The product was 20.4 g (64.8%) of pure hydrochloride of DL-threo-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIa), m.p. 195°.

	Found %	C 42.14; H 4.79; N 4.44; Cl 11.75; 33.83
$C_{11}H_{14}O_3NCl_3$.	Calculated %	C 41.99; H 4.49 N 4.45 Cl 11.27; 33.81

DL-threo-2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol (Va). Ethyl acetate (90 ml) was added to a solution of 15.75 g (0.05 mole) of the hydrochloride of O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (V a) in 45 ml of water. The mixture was stirred at 25°, and 3.45 g (0.025 mole) of anhydrous potassium carbonate was added in small portions over a period of five minutes. The mixture was stirred for five minutes, and the aqueous layer was then separated and extracted four times with 25-ml portions of ethyl acetate. The extract was dried and evaporated, when 13.2 g of a light-yellow oil was obtained which solidified after some hours (yield 95%). Recrystallization from 50% aqueous ethanol yielded 11.8 g (78%) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), m.p. 90°. After two further recrystallizations the melting point rose to 94-95°.

	Found %	C 47.68; H 4.79; N 5.37; Cl total 25.05
$C_{11}H_{13}O_3Cl_2$.	Calculated %	C 47.50; H 4.71; N 5.04; Cl total 25.50

DL-threo-2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol Diacetic Ester. A mixture of 11.19 g (0.04 mole) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), 10 ml of anhydrous pyridine, and 12 ml of acetic anhydride was heated at 100° for 30 minutes and then evaporated down under reduced pressure. After a few days the reddish-yellow oily residue solidified. Crystallization of the residue from 20 ml of 60% ethanol yielded 12.2 g (83%) of crystalline DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol, m.p. 93-95°.

	Found %	C 49.91; H 4.52; N 3.87; Cl 19.65
$C_{15}H_{17}O_5NCl_2$.	Calculated %	C 49.74; H 4.73; N 3.87; Cl 19.58

U. S. Patent 2538766 (Example 2b) refers to this compound, but no yield and no physical constants are given.

DL-threo-O^3-Acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb). Acetic anhydride (8 ml) was added to 5.56 g (0.02 mole) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), and the mixture was maintained at 70° for 15 minutes. The slightly yellowish oil that remained after removal of acetic anhydride by distillation solidified after 24 hours (6.3 g). This substance was dissolved in 24 ml of ethyl acetate and crystallization was promoted by addition of 36 ml of petroleum ether. The product was 4.6 g (72%) of DL-threo-O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb), m.p. 97-99°, raised by recrystallization to 100-101°.

Found %: C 48.67; H 4.68; N 4.41; Cl 21.89
$C_{13}H_{15}O_4NCl_2$. Calculated %: C 48.76; H 4.72; N 4.37; Cl 22.18

Hydrochloride of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb). To an ice-cooled solution of 3.2 g (0.01 mole) of DL-threo-O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol in 10 ml of absolute ether, 3.2 ml of a solution of HCl (0.02 mole) in absolute ethanol was added, and the mixture was set aside at 0°. On the next day the crystals that had formed were centrifuged off and washed three times with 3-ml portions of a 1 : 20 mixture of absolute ethanol and absolute ether. The product was 2.6 g (74%) of the hydrochloride of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb), m.p. 169-172°, raised to 187° by recrystallization from a 1 : 2 mixture of absolute ethanol and absolute ether.

Found %: C 43.52; H 4.75; N 4.23; Cl 30.18; 9.93
$C_{13}H_{16}O_4NCl_3$. Calculated %: C 43.78; H 4.52. N 3.93; Cl 29.83; 9.95

Nitrate of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb). A solution of 0.94 g (0.015 mole) of nitric acid in 5 ml of dioxane was added to an ice-cooled solution of 3.2 g (0.01 mole) of O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb) in 10 ml of dioxane. The reaction mixture was set aside for some days at 0°, and a white microcrystalline substance separated, which was filtered off and washed with absolute ether. The product was 2.9 g (75.5%) of the nitrate of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb), m.p. 122-124°. Recrystallization from 12 ml of absolute ethanol yielded the pure substance, which melted at 126-128°.

Found %: C 41.08; H 4.38; N 7.22; Cl 18.87
$C_{13}H_{15}O_7N_2Cl_2$. Calculated %: C 40.75; H 4.21; N 7.31; Cl 18.51

Hydrochloride of DL-erythro-2-Amino-3-chloro-3-phenyl-1-propanol. 2-Acetamido-3-hydroxypropiophenone isolated from the racemic mixture remaining after the preparation of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol was reduced and yielded a crystalline substance melting at 90-95°. This substance (30 g) was added to 90 ml of thionyl chloride, the mixture being cooled with ice. The mixture was allowed to stand for 15 minutes at room temperature, and 90 ml of water was then added dropwise. It was then heated for two hours at 100°, cooled, and set aside for 12 hours at −20°. A white crystalline substance (14.6 g) separated. Recrystallization from a small amount of water yielded 11.8 g (28.2%) of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol, m.p. 187-188°.

Found %: C 48.96; H 5.95; N 6.41; Cl total 31.93; 16.19
$C_9H_{13}ONCl_2$. Calculated %: C 48.66; H 5.90; N 6.31; Cl total 31.93; 15.97

The mother liquor was evaporated down, and the residue was crystallized from a 1 : 1 mixture of absolute ethanol and absolute ether, when the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol (IV), m.p. 192°, was obtained. The melting point of 178° that is given in U. S. Patent 2513346 (Example 2d) probably corresponds to a mixture of two substances indicated above.

DL-erythro-3-Chloro-2-(2,2-dichloroacetoamido)-3-phenyl-1-propanol. Methyl dichloroacetate (11 ml i.e. 14.3 g) was added to a solution of 4.4 g (0.02 mole) of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol. The mixture was stirred vigorously at 8-10°, and over a period of about 30 minutes 6 ml of 40% caustic soda solution was added dropwise in such a way that the pH of the solution remained between 6 and 8. The layers were separated, and the aqueous layer was extracted five times with 50-ml portions of ethyl acetate. The combined extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure. The oily residue was dissolved in 15 ml of ethyl acetate, the resulting solution was treated with bone charcoal, and crystallization was effected by addition of 60 ml of absolute ether, when 4.35 g (69%) of DL-erythro-3-chloro-2-(2,2-dichloroacetamido)-3-phenyl-1-propanol monohydrate, m.p. 147°, was obtained.

Found %: C 41.91; H 4.61; N 4.56; Cl 33.78
$C_{11}H_{12}O_2NCl_3 \cdot H_2O$. Calculated %: C 41.99; H 4.49; N 4.45; Cl 33.81

N to O Migration of the Acyl Residue. DL-erythro-3-Chloro-2-(2,2-dichloroacetamido)-3-phenyl-1-propanol monohydrate (0.28 g, i.e. 0.00112 mole) was dissolved in 5 ml of absolute ethanol, and, under ice-cooling, 0.34 ml of a 32.18% solution of HCl in absolute ethanol (0.00336 mole) was added. After a few minutes 0.22 g of white crystals of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol dichloroacetic ester, m.p. 194°, were precipitated.

Found %: C 39.52; H 4.12; N 4.30; Cl total 42.18
$C_{11}H_{13}O_2NCl_4$. Calculated %: C 39.67; H 3.93; N 4.21; Cl total 42.58

Found % Cl^- 10.72
Calculated % Cl^- 10.64

DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol Diacetic Ester. 2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol diacetic ester (7.24 g, i.e. 0.02 mole) was dissolved in 20 ml of absolute chloroform, and this solution was added dropwise over a period of 50 minutes, with rapid stirring and cooling to 0°, to a mixture of 10 ml (18.2 g) of concentrated sulfuric acid and 1.45 ml (2.02 g; 0.022 mole) of nitric acid. The reaction mixture was stirred for 30 minutes and then poured in a thin stream onto 45 g of ice. The layers were separated, and the aqueous layer was extracted with four 8-ml portions of chloroform. The combined chloroform extract was shaken with two 6-ml portions of 10% sodium bicarbonate solution and with 5 ml of water. The chloroform solution was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. Recrystallization from 80% ethanol yielded 3.5 g (43%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol diacetic ester, m.p. 138-139° after repeated recrystallization.

Found % C 44.08; H 4.24; N 6.94; Cl 17.35
$C_{15}H_{18}O_7N_2Cl_2$. Calculated % C 44.24; H 3.96; N 6.88; Cl 17.41

DL-threo-2-Amino-1-p-nitrophenyl-1,3-propanediol (IX). DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol diacetic ester (1.02 g, i.e. 0.0025 mole) was boiled for four hours with 12 ml of 5% hydrochloric acid. The mixture was cooled and extracted with two 12-ml portions of ether. The aqueous phase was freed from traces of ether and made slightly alkaline (pH 8.5) with 40% caustic soda solution. Very quickly 0.455 g (86.5%) of white crystals of DL-threo-2-amino-1-p-nitrophenyl-1,3-propanediol (IX), m.p. 129-131°, appeared. Recrystallization from water raised the melting point to 142-143°.

DL-Chloramphenicol (Levomycetin, Synthomycin). DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa). a) DL-threo-2-Amino-1-p-nitrophenyl-1,3-propanediol (IX) (2.12 g, i.e. 0.01 mole) was dissolved in 40 ml of ethanol, and 2 ml of a 30% solution of HCl in absolute ether was added. The solution was evaporated to dryness, and the residue was dissolved in 24 ml of water. Methyl dichloroacetate (8 ml) was added, and the mixture was stirred vigorously at 8-10° while 4.5 ml of 36% caustic soda solution was added over a period of 50 minutes in such a way that the pH of the reaction mixture remained between 6 and 8. After reaction had been proceeding for ten minutes, 5 ml of methanol was added. After the addition of alkali was complete, the solution was freed from methanol at 40° and 2 mm pressure and was then extracted with six 20-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The light-yellow oily residue was dissolved in 8 ml of hot ethyl acetate and caused to crystallize by addition of 4 ml of petroleum ether. The product was 2.23 g (72%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), melting after recrystallization at 152-153°. There was no depression in a mixture test with authentic chloramphenicol [6].

Found % C 40.72; H 3.86; N 8.78; Cl 22.12
$C_{11}H_{12}O_5N_2Cl_2$. Calculated % C 40.88; H 3.74; N 8.67; Cl 21.95

b) DL-threo-2-(2,2-Dichloroacetamido)-1-nitrophenyl-1,3-propanediol diacetic ester (1 g, i.e. 0.0025 mole) was dissolved in 50 ml of acetone. The solution was cooled to −7 to −8° and was stirred vigorously while 100 ml of 0.1 N NaOH, cooled to +2°, was added dropwise. The temperature of the solution was maintained at −10° for the next two hours. The solution was then titrated to Methyl orange with 0.2 N HCl. Acetone was removed at 2 mm pressure (30°), and the residue was extracted with ten 50-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Two recrystallizations of the oily residue from ethyl acetate yielded 0.62 g of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), m.p. 151-153°, undepressed by admixture of authentic chloramphenicol [6].

c) The nitrate of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb) (10 g) was added at 0-5° with vigorous stirring to 30 ml of nitric acid (sp. gr. 1.52). After one hour the reaction mixture was poured into cold water containing potassium bicarbonate and calcium carbonate. The reaction product was extracted with five 50-ml portions of chloroform. The chloroform solution, after being dried and evaporated, yielded 4.02 g of an oily residue, which was dissolved in 220 ml of acetone. Cooled 0.1 N NaOH (440 ml) was added dropwise at −7 to −8°, and the mixture was maintained at −14° for two hours, after which it was neutralized with 0.2 N HCl. Acetone was removed at 30° (2 mm), and the residue was extracted with ten 60-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated. The oily residue was crystallized from 30 ml of 1 : 1 mixture of absolute ethyl acetate and absolute petroleum ether. The product was 2.12 g (25.5%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), m.p. 151-153.5°, undepressed by admixture with authentic chloramphenicol [6].

This investigation was aided by gifts of materials from the "Quinoin" pharmaceutical works and the Research Institute of the Pharmaceutics Industry. Microanalyses were carried out in our department by Dr. Eva Fodor-Varga, K. Lang, and R. Minarovich, with the help of technicians Imre Sabo and Lyuda Sabadi.

LITERATURE CITED

[1] V. Bruckner, Ann. 518, 226 (1935).

[2] V. Bruckner, A. Kramli, J. Prakt. Chem. 143, 2, 288(1935); 148, 5, 177 (1937).

[3] V. Bruckner, G. Fodor, Ber. 76, 466 (1943); G. Fodor, Ber. 76, 121 (1943); V. Bruckner, G. Fodor, I. Kiss, J. Kovacs, J. Chem. Soc. 1948, 885; G. Fodor, J. Kiss, M. Szerkerke, J. org. Chem. 15, 227 (1950). I. Kovacs, Pseudonitrosites of some Derivatives of Cinnamyl Alcohol, Doctorate Thesis, Szeged, 1943.

[4] E. Cherbuliez, Fr. Neumeir, H. Lozeron, Helv. 14, 191 (1931).

[5] Lott, US.Pat. 2103268.

[6] J. Controulis, M. C. Rebstock, H. M. Crooks, J. Am. Chem. Soc. 71, 2463 (1949).

[7] I. Kollonich, Report on Conference of the Society of Hungarian Chemists, Debreczen, 27. IX, 1953.

[8] L. M. Long, H. D. Troutman, J. Am. Chem. Soc., 71, 2469 (1949).

[9] a) G. Fodor, J. Kiss, Nature 163, 287 (1944); b) G. Fodor, J. Kiss, G. Ohegyi, J. org. Chem. 14, 336 (1949); c) G. Fodor, J. Kiss, M. Szekerke, J. org. Chem. 15, 227 (1950).

[10] G. Fodor, J. Kiss, L. Sallay, Nature 167, 690 (1951); J. Chem. Soc. 1951, 1858.

[11] K. Freudenberg, E. Schoffel, E. Braun, J. Am. Chem. Soc. 54, 234 (1932).

[12] K. J. Freudenberg, F. Nikolai, Ann. 510, 223 (1934); Leithe, Ber. 65, 660 (1932).

[13] K. Mislow, J. Am. Chem. Soc. 73, 3954 (1951).

[14] G. Carrara, G. Weitnauer, Gazz. Chim. Ital. 79, 856 (1949).

[15] K. Vogler, Helv. 33, 2111 (1950).

[16] J. D. Dunitz and J. E. Leonard, J. Am. Chem. Soc. 72, 4276 (1950).

[17] N. A. Preobrazhensky and E. I. Genkin, Chemistry of Organic Drugs, Satate Chem. Press, Moscow, 1953, pp. 545-546.

[18] a) Berichte Schimmel and Co. 1922, 5-166; C. 1929, IV, 764; b) M. Bourguel, Bull. 45, [4], 1067 (1929).

Received January 3, 1955

Institute of Organic Chemistry
Szeged University
Hungary

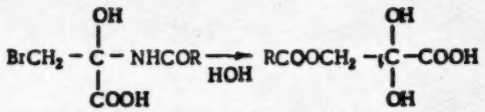
BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 7. REACTIONS OF N-ACYL-2,3-DIHALOALANINES. (ACYLOXY)PYRUVIC ACIDS

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

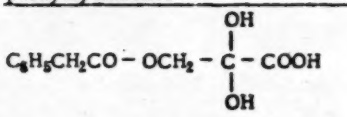
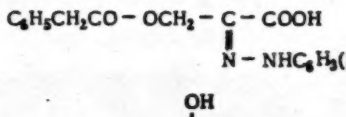
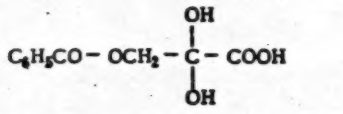
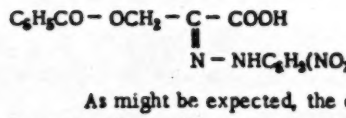
In a previous communication [1] we have described the formation and properties of N-acyl-3-halo-2-hydroxyalanines. Further investigation of the properties of these acids has shown that they are readily converted into new (acyloxy)pyruvic acids. When 3-bromo-2-hydroxy-N-(phenylacetyl)alanine and N-benzoyl-3-bromo-2-hydroxyalanine were treated with aqueous sodium bicarbonate, at first the acids were dissolved, and then the sparingly soluble sodium salts of the corresponding (acyloxy)pyruvic acids were precipitated; and from these the free acids (I and II) were liberated in the form of their hydrates by the action of 25% sulfuric acid.



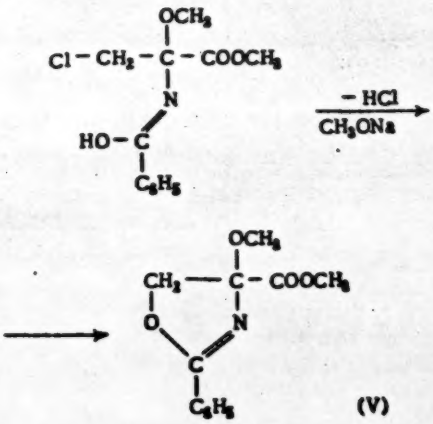
(R = C_6H_5, $CH_2C_6H_5$).

(Acyloxy)pyruvic acids are readily soluble in water and in most organic solvents. They can be recrystallized from chloroform or dichloroethane. In alkaline solution they give the reddish-violet color characteristic for hydroxypyruvic acid. 2-4-Dinitrophenylhydrazine immediately gives precipitates of the corresponding 2,4-dinitrophenylhydrazones (III) and (IV), identical with the 2,4-dinitrophenylhydrazones obtained by acid hydrolysis of N-acyl-2,3-dibromoalanines [2].

TABLE

(Acyloxy)pyruvic acids and their 2,4-dinitrophenylhydrazones		M.p. (°C)
	(I)	57 – 58
	(III)	169 – 170
	(II)	68 – 70
	(IV)	168 – 173

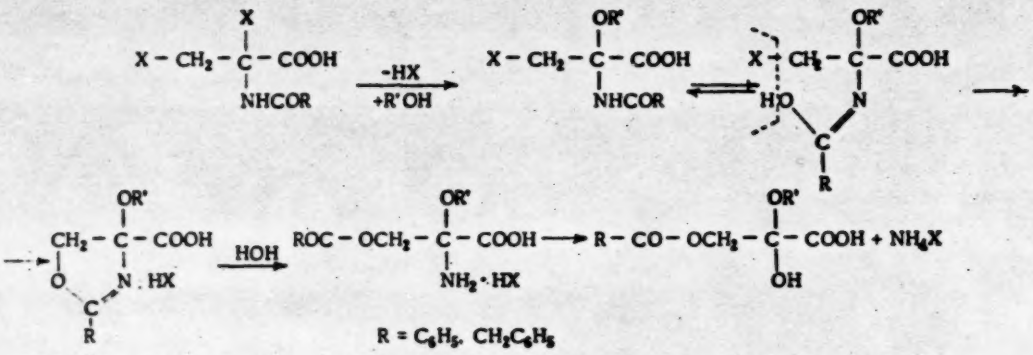
Investigation of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine [1] has shown that the conversion of N-acyl-2,3-dihaloalanines and N-acyl-3-halo-2-hydroxyalanines into derivatives of (acyloxy)pyruvic acids proceeds through the intermediate formation of oxazoline derivatives. When the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine was treated with an equimolecular amount of sodium methoxide, the methyl ester of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid (V), m.p. 56°, was isolated.



As might be expected, the oxazoline (V) was found to be extremely sensitive toward acids. Thus, we were able to isolate the stable sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid after hydrolysis of the ester group, but all attempts to convert this into the free acid were unsuccessful. Acidification of the sodium salt resulted in cleavage of the oxazoline ring and the only final hydrolysis product was the (acyloxy)pyruvic acid. Hence, in reactions in aqueous media both N-acyl-2,3-dibromoalanines and N-acyl-3-bromo-2-hydroxyalanines generally yield hydroxypyruvic acid or its derivatives.

N-Acyl-2,3-dichloroalanines and N-acyl-3-chloro-2-hydroxyalanines were found to be more stable to hydrolysis, and the conversion of N-benzoyl-3-chloro-2-hydroxyalanine, for example, was found to occur only under the action of a stronger base (N NaOH).

The fact of the formation of the methyl ester of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid enables us to represent the conversion of halogen derivatives of N-acylalanines into derivatives of (acyloxy)pyruvic acids in the following way:

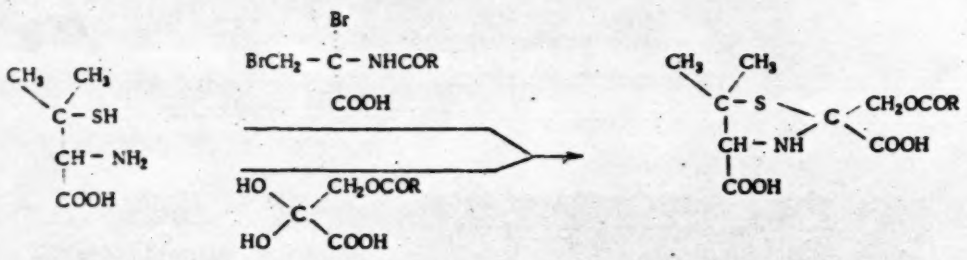


R = C_6H_5, $CH_2C_6H_5$

R' = H, CH_3, C_2H_5

A certain analogy to the rearrangement that we have observed is to be found in the migration of an acyl group from nitrogen to oxygen in hydroxy amines [3, 4, 5].

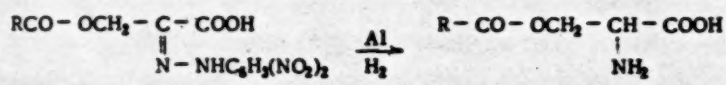
The above-described transformations of N-acyl-2,3-dihaloalanines occur also when these compounds are condensed with 3,3-dimethylcysteine. Reaction of 3,3-dimethylcysteine with N-benzoyl-2,3-dibromoalanine, with 2,3-dibromo-N-(phenylacetyl)alanine, and with 3-bromo-2-hydroxy-N-(phenylacetyl)alanine over a wide pH range (2-8) yields mainly 2-(acyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acids (VI and VII), identical to the acids obtained by the direct condensation of 3,3-dimethylcysteine with (acyloxy)pyruvic acids:



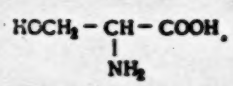
(VI) R = $CH_2C_6H_5$; (VII) R = C_6H_5.

Cleavage of 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid with alcoholic mercuric chloride yielded the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid.

A possible method for proving the structure of the (acyloxy)pyruvic acid would be an examination of the product of the reduction of its 2,4-dinitrophenylhydrazone, which should yield an O-acylserine, or serine itself if reduction were accompanied by hydrolysis of the ester grouping:



or



(R = $CH_2C_6H_5$; C_6H_5).

A similiar example of the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid was recently described by Sprinsson and Chargaff [6], who did in fact isolate serine in 30% yield. In contrast with this

experiment on the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, the reduction of the 2,4-dinitrophenylhydrazones of (acyloxy)pyruvic acid, that we have prepared unexpectedly resulted in the isolation of alanine. This result caused us to make a more detailed study of the reduction products, not only those formed in Sprinsson and Chargaff's experiment, but also those obtained from the 2,4-dinitrophenylhydrazones of (acyloxy)-pyruvic acid.

An investigation of the reduction products obtained in these reactions with the aid of partition chromatography showed that in the reduction of 2,4-dinitrophenylhydrazones of (acyloxy)pyruvic acids, not only alanine – the main reaction product – but also serine and O-acylserine were formed:

$$R-CO-OCH_2-\underset{\underset{N-NHC_6H_3(NO_2)_2}{\|}}{C}-COOH \xrightarrow[H_2]{Al} CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH \quad \text{and traces of}$$

$$RCO-OCH_2-\underset{\underset{COOH}{|}}{CH}-COOH \quad \text{and} \quad HO-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH,$$

(R = $CH_2C_6H_5$, C_6H_5).

In the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, the main reaction product is indeed serine, as stated by Sprinsson and Chargaff [6], but alanine, which they did not detect, is also present:

$$HO-CH_2-\underset{\underset{N-NHC_6H_3(NO_2)_2}{\|}}{C}-COOH \xrightarrow[H_2]{Al} HO-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH \quad \text{and traces of}$$

$$CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH$$

Thus, in this investigation we have found examples of the reduction of hydroxymethyl and acyloxymethyl groups to CH_3 groups by aluminum amalgam. This result is the consequence of the structural peculiarities of hydrazones of hydroxypyruvic acid. Unlike the hydrazones of (acyloxy)- and hydroxy-pyruvic acids, O-acylserine does not yield alanine under the same conditions. Hence, the presence of the α-hydrazone grouping greatly affects the character of the hydroxy or acyloxy group, making them capable of undergoing exhaustive reduction (to the CH_3 group) under conditions under which alcohols and esters are not reduced. Similar behavior has been observed by Piloty and Ruff [7], who obtained isopropylamine by the reduction of the oxime of dihydroxyacetone:

$$HOCH_2-\underset{\underset{NOH}{\|}}{C}-CH_2OH \xrightarrow[H_2]{Na} CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

The two examples of the reduction of hydroxy and acyloxy groups found in this investigation and the reduction of the oxime of dihydroxyacetone to isopropylamine are examples of what is probably a general rule of the ready reduction of the hydroxy groups of oximes and hydrazones of α-hydroxy carbonyl compounds.

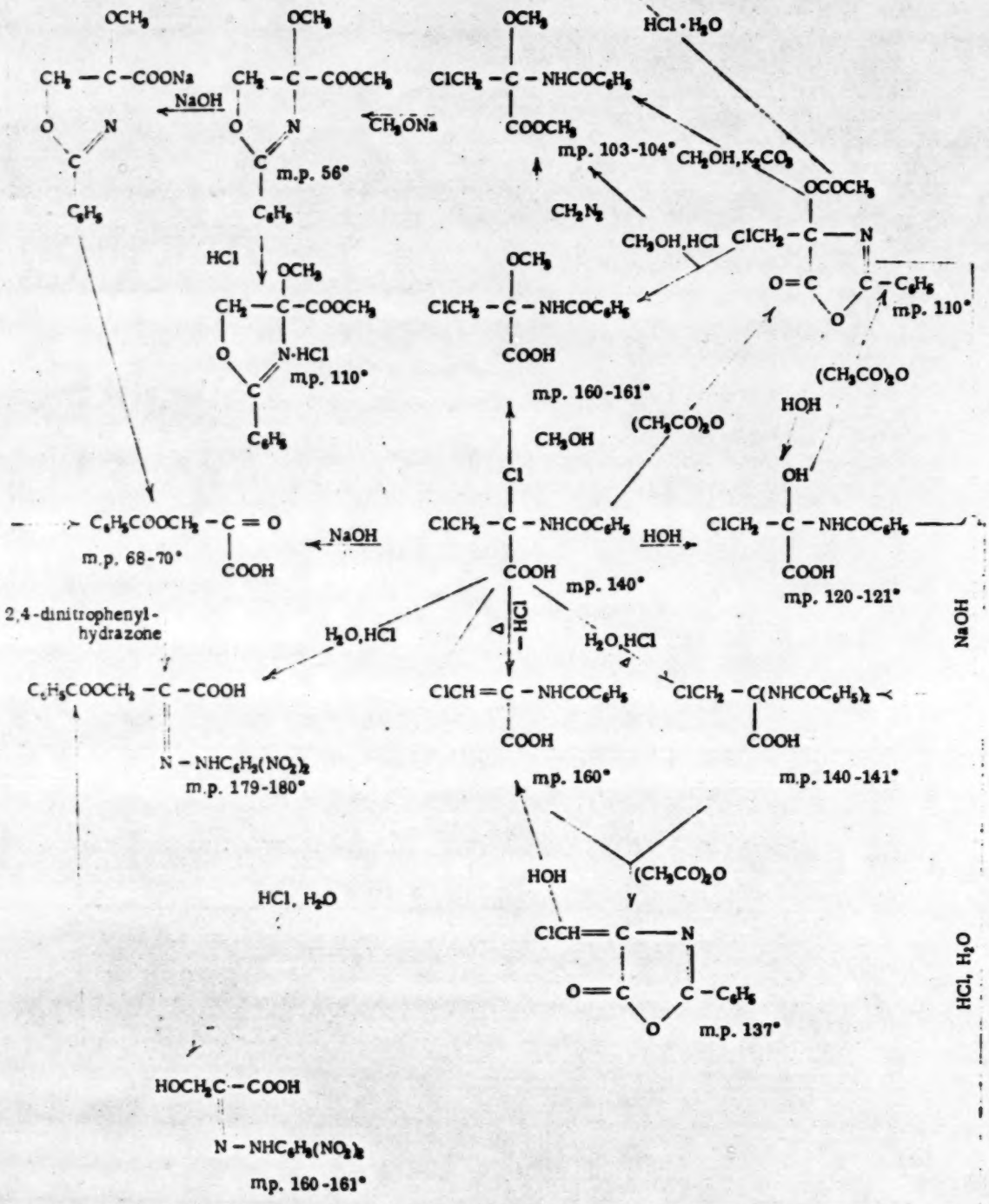
It should be noted that reduction of the hydrazones of (acyloxy)pyruvic acids gives an appreciably higher yield of alanine than the reduction of the corresponding hydroxy compounds.

The formation of (acyloxy)pyruvic acids from N-acyl-2,3-dihaloalanines described in this communication forms the connecting link between the various separate groups of reactions of these complex multifunctional compounds which we have examined previously [1, 2, 8]. The general cycle of transformations is given in the scheme below, the reactions of N-benzoyl-2,3-dichloroalanine being taken as an example. (See Scheme p. 404).

EXPERIMENTAL

Hydrate of (Phenylacetoxy)pyruvic Acid (I). 2,3-Dibromo-N-(phenylacetyl)alanine (4.5 g, i.e. 0.0125 mole) was treated with excess of a saturated aqueous solution of sodium bicarbonate (2.1 g, i.e. 0.025 mole, in 20 ml of water). The alkaline solution was acidified to pH 1.5 with concentrated hydrochloric acid. After a short time the crystalline precipitate that formed was filtered off. The product was 0.9 g (24.0%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, m.p. 105-106°.

The acid mother liquor was evaporated to dryness under reduced pressure. The residue was extracted with ether. Ether was allowed to evaporate until crystallization began. The crystals were filtered off, washed with a


NaOH
CH3ONa
m.p. 56°
HCl
m.p. 110°
m.p. 103-104°
CH2OH,K2CO3
CH2N2
CH3OH,HCl
m.p. 110°
m.p. 160-161°
(CH3CO)2O
CH3OH
m.p. 68-70°
NaOH
m.p. 140°
HOH
m.p. 120-121°
2,4-dinitrophenyl-hydrazone
H2O,HCl
-HCl
m.p. 179-180°
m.p. 160°
m.p. 140-141°
HCl, H2O
m.p. 137°
NaOH
HCl, H2O
m.p. 160-161°

little benzene, and then chloroform, and finally crystallized from chloroform. The product was 0.5 g (17%) of the hydrate of (phenylacetoxy)pyruvic acid in the form of petal-shaped crystals, m.p. 57-58°.

	Found %:	C 54.87; H 4.93
$C_{11}H_{12}O_5$.	Calculated %:	C 55.00; H 5.0

The hydrate of (phenylacetoxy)pyruvic acid was found to be very soluble in water, alcohol, and ether, and it readily crystallized from chloroform and dichloroethane. In alkaline solution it gave a reddish-violet color with ferric chloride. With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2N HCl an aqueous solution of the hydrate of (phenylacetoxy)pyruvic acid immediately gave a crystalline hydrazone, m.p. 168-170° (from alcohol), identical with the 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid isolated in the hydrolysis of 2,3-dibromo-N-(phenylacetyl)alanine [2].

	Found %:	C 50.52; H 3.49
$C_{17}H_{14}O_8N_4$.	Calculated %:	C 50.74; H 3.48

The hydrate of (phenylacetoxy)pyruvic acid is converted by sodium bicarbonate solution into the sodium salt, which is sparingly soluble in water. The free acid is liberated when the salt is treated with 25% sulfuric acid.

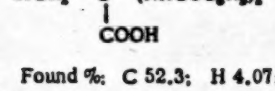
Hydrate of (Benzoyloxy)pyruvic Acid (II). N-Benzoyl-2,3-dibromoalanine (8 g, i.e. 0.022 mole) was treated with a saturated aqueous solution of sodium bicarbonate (3 g, i.e. 0.037 mole, in 30 ml of water). The precipitate was filtered off; it consisted of 2.7 g (44.2%) of N-benzoyl-3-bromo-2-hydroxyalanine, m.p. 92-93°. The filtrate was set aside in a refrigerator. On the next day the crystalline precipitate was filtered off (yielding Filtrate I), washed with a little water, and dried in a vacuum desiccator over phosphoric oxide. The product was 2 g of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid, which crystallized very satisfactorily from hot water in the form of clear gleaming crystals. The free hydrate of (benzoyloxy)pyruvic acid was liberated from its sodium salt by means of 25% sulfuric acid. A day elapsed after the acidification of the clear solution before a precipitate of the free acid formed. The precipitate was filtered off, washed with a little water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.7 g of the hydrate of (benzoyloxy)pyruvic acid, m.p. 68-70° (from chloroform).

	Found %:	C 52.88; H 4.47
$C_{10}H_{10}O_5$.	Calculated %:	C 53.0; H 4.42

The hydrate (II) was found to be readily soluble in water, alcohol, and ether, and could be crystallized from chloroform and dichloroethane. With ferric chloride an alkaline solution of the hydrate of (benzoyloxy)pyruvic acid gave the reddish-violet color that is characteristic for hydroxypyruvic acid. When the solution was heated for three minutes with 0.5 N NaOH, the reaction with ferric chloride was no longer given. The solution was cooled and acidified with 25% sulfuric acid, and the precipitate that formed was filtered off and dried. The product was benzoic acid, m.p. 121-122° (from water), undepressed by admixture with known benzoic acid. With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl the hydrate (II) gave a hydrazone melting at 168-173°, identical with the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid isolated in the acid hydrolysis of N-benzoyl-2,3-dibromoalanine [2].

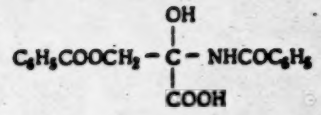
	Found %:	C 49.36; H 3.17; N 14.37
$C_{18}H_{12}O_8N_4$.	Calculated %:	C 49.48; H 3.09; N 14.4

Filtrate I was evaporated to dryness under reduced pressure, and the residue was treated with 25% sulfuric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated until crystallization began. The precipitate was filtered off and found to be 1.1 g of a substance with an extended melting range. After repeated reprecipitation from a sodium bicarbonate solution with acid and fractional crystallization of the sodium salts from water, we succeeded in isolating some more hydrate of (benzoyloxy)pyruvic acid, m.p. 68-70° (0.2 g; the total yield of the hydrate (II) was 17.6%) and also the new 2,2-bis(benzamido)-3-bromopropionic acid, m.p. 124°:



	Found %:	C 52.3; H 4.07; N 7.59; Br 21.47
$C_{17}H_{15}O_4N_2Br$.	Calculated %:	C 52.1; H 3.83; N 7.2; Br 22.4

In addition to this an acid having a double melting point, 90° and 114°, was isolated. It was close in properties to the hydrate of (benzoyloxy)pyruvic acid, but contained nitrogen. It is probable that it was inadequately purified N-benzoyl-3-(benzoyloxy)-2-hydroxyalanine.



Found %: N 4.17

$C_{17}H_{15}O_6N$. Calculated %: N 4.25

With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl the acid melting at 90° and 114° gave a 2,4-dinitrophenylhydrazone melting at 168-170°. A mixture test with the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid showed no depression.

Methyl Ester of 4-Methoxy-2-phenyl-2-oxazoline-4-carboxylic Acid (V). A solution of 0.54 g (0.002 mole) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine in 5 ml of absolute methanol was mixed with 2.4 ml of a solution of sodium methoxide (0.002 mole). After two hours at room temperature the solution was evaporated to dryness under reduced pressure. The residue was extracted with absolute ether, and the ether was distilled off. The product was the methyl ester of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid, m.p. 56°.

Found %: C 61.29; H 5.47; N 6.07

$C_{12}H_{13}NO_4$. Calculated %: C 61.27; H 5.50; N 5.95

Treatment of (V) with alcoholic HCl in absolute ether gave a crystalline hydrochloride, m.p. 110°, which decomposed very readily.

Sodium Salt of 4-Methoxy-2-phenyl-2-oxazoline-4-carboxylic Acid. To 0.27 g (0.001 mole) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine in 2 ml of methanol, 1 ml of 2 N methanolic NaOH (0.002 mole) was added, and the mixture was set aside for two hours at room temperature. Precipitated sodium chloride was filtered off, and the filtrate was evaporated to half bulk under reduced pressure. The precipitated sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid was filtered off and washed with a little alcohol. The product was 0.15 g of the sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid.

Found %: N 5.38

$C_{11}H_{10}NO_4Na$. Calculated %: N 5.75

The sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid was found to be readily soluble in alcohol and in water. It was not found possible to isolate the free acid from the sodium salt; when an aqueous solution was acidified with the equivalent amount of sulfuric acid, after some time a precipitate of the sodium salt of (benzoyloxy)pyruvic acid formed.

5,5-Dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic Acid (VI). 3-Bromo-2-hydroxy-N-(phenylacetyl)alanine (0.6 g, i.e. 0.002 mole) was added to a solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine and 0.16 g (0.002 mole) of sodium bicarbonate in 5 ml of water. The mixture (pH 4) was set aside for 12 hours at room temperature. On the next day a precipitate had formed of the monosodium salt of 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, m.p. 187-190° (dec.). Acidification of the mother liquor with N H_2SO_4 yielded a precipitate of 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, readily soluble in alcohol, ether, and acetone, sparingly soluble in benzene and chloroform. The acid was purified by dissolving it in acetone, adding an equal volume of water, and leaving the solution to the next day. The acid (VI) then melted with decomposition at 166-167°.

Found %: C 53.9; H 5.5; S 9.1

$C_{18}H_{19}O_6NS$. Calculated %: C 54.3; H 5.3; S 9.06

The neutralization equivalent was found to be 177 (molecular weight 353).

The monosodium salt was acidified with sulfuric acid and yielded the free acid (VI), m.p. 167-168° (dec.). The total yield of the acid (VI) was 80%.

Similar results were obtained also with 2,3-dibromo-N-(phenylacetyl)alanine in presence of two molecular proportions of sodium bicarbonate. With excess of diazomethane in ether solution 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid formed what appeared to be the dimethyl ester of 3,5,5-trimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, m.p. 101-102° (from ether).

Found %: C 58.02; H 6.6; S 8.14

$C_{19}H_{25}O_6NS$. Calculated %: C 57.7; H 6.3; S 8.1

2-(Benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic Acid (VII). a) N-Benzoyl-2,3-dibromoalanine (4.3 g, i.e. 0.012 mole) was added to a solution of 1.9 g (0.012 mole) of 3,3-dimethylcysteine in 20 ml of water, and the mixture (pH 2) was set aside for 12 hours at room temperature. The precipitate formed was filtered off and washed with a little water. The product was 3.45 g (80.6%) of the acid (VII); 3 g of this was dissolved in 10 ml of acetone, 20 ml of water was added, and the mixture was set aside until the next day, when 2.5 g of the acid (VII) melting with decomposition at 165-166° was obtained.

2-(Benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid is readily soluble in alcohol, ether, and acetone, sparingly soluble in chloroform and cold water; it can be crystallized from hot water. In the cold it is insoluble in 2 N HCl, and at the boil it is decarboxylated. It may be titrated iodometrically in the same way as penicilloic acid [9].

	Found %	C 52.7; H 5.2; S 9.3; N 4.3
$C_{15}H_{17}O_5NS$.	Calculated %	C 53.0; H 5.0; S 9.4; N 4.1

b) To a solution of 1.5 g (0.01 mole) of 3,3-dimethylcysteine in 20 ml of water, 3 g (0.04 mole) of sodium bicarbonate and 3.4 g (0.01 mole) of N-benzoyl-2,3-dibromoalanine were added. The mixture was set aside at room temperature for 12 hours, and was then heated for five hours at 40° (pH 8). The ferric chloride test for the mercapto group was positive. The mixture was cooled, and the precipitate present was filtered off and washed with water. The product was 0.8 g of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid. Acidification of the mother liquor with N H_2SO_4 gave a very slight precipitate of 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid.

Treatment of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid with 25% sulfuric acid yielded the free hydrate of the acid, m.p. 68-70° (from chloroform), identical with the hydrate (II). When 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid was treated with mercuric chloride in presence of 2,4-dinitrophenylhydrazine, the hydrazone of (benzoyloxy)pyruvic acid, m.p. 167-168° and identical with the hydrazone (IV), was obtained.

Reduction of 2,4-Dinitrophenylhydrazones Derived from Pyruvic Acid. 1) A suspension of 3.8 g (0.01 mole) of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid in 100 ml of 80% ethanol was treated with freshly prepared activated aluminum (prepared with the aid of $HgCl_2$ by Adkin's method from 10 g of aluminum). The mixture was stirred at 20° for 30 minutes, and stirring was continued overnight at room temperature. On the next day the dark-brown solution was filtered, and the aluminum hydroxide was carefully washed on the filter with 300 ml of hot water. The dark-brown solution was decolorized with animal charcoal and evaporated to dryness under reduced pressure. The residue was dissolved in the least possible volume of water, absolute alcohol was added until a turbidity appeared, and the mixture was set aside in a refrigerator. On the next day the crystalline precipitate was filtered off and dried; it was 0.25 g (28%) of alanine, melting with decomposition at 290-292° and showing no depression in a mixture test with known alanine. The mother liquor from the alanine separation was evaporated to dryness at room temperature, and the residue was dissolved in the least possible amount of water and analyzed by partition chromatography on paper. The developed chromatogram showed the presence of alanine, serine, and O-benzoylserine.

2) The 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid (1 g) was reduced with amalgamated aluminum in the manner described above. The solution, after decolorization with charcoal, was evaporated to low bulk and analyzed by partition chromatography on paper. The developed chromatogram showed the presence of alanine, serine, and O-(phenylacetyl)serine.

3) The above-described method of reduction with amalgamated aluminum was applied to 1 g of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid (prepared by Sprinsson's method [6] from bromopyruvic acid). The solution, after evaporation to low bulk, was analyzed by partition chromatography on paper. The developed chromatogram showed the presence not only of serine, but also of alanine.

4) O-Benzoylserine (0.7 g) was subjected to the aluminum-amalgram reduction treatment described above for the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid. Only serine was isolated, and no other substance was detected on the chromatogram.

SUMMARY

1. It is shown that, over a wide pH range, N-acyl-2,3-dihaloalanines are converted by water into (acyloxy)pyruvic acids with intermediate formation of 2-aryl (or alkyl)-4-hydroxy-2-oxazoline-4-carboxylic acids.

2. It is shown that the ability of α-acetoxy and α-hydroxy groups in hydrazones and oximes of α-hydroxy carbonyl compounds to undergo exhaustive reduction when treated with metal amalgams and water forms a general rule.

LITERATURE CITED

[1] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 271.•

[2] O. V. Kildisheva, L. P. Rasteiken, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 260. ••

[3] M. Bergmann, A. Mickely, Z. phys. Chem. 140, 128 (1924).

[4] E. Fry, J. org. Chem. 14, 887 (1949); 15, 438 (1950).

[5] E. Baltazz et al., Chem. Ind. No. 22, 541 (1953).

[6] D. Sprinsson, E. Chargaff, J. Biol. Chem. 164, 417 (1946).

[7] Piloty, O. Ruff, Ber. 30, 1664 (1897).

[8] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 282. •••

[9] J. Alicino, Ind. Eng. Chem. (Anal. Ed.), 18, No. 20, 619, 1946.

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

• Consultant's Bureau Translation, p 241.

•• Consultant's Bureau Translation, p 231.

••• Consultant's Bureau Translation, p 251.

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 8. ALKYLATION AND ACYLATION OF CYSTEINE AND 3,3-DIMETHYLCYSTEINE BY DERIVATIVES OF N-ACYL-3-HALOALANINES

I. L. Knunyants and V. V. Shokina

It was shown in a previous communication [1] that 3,3-dimethylcysteine is readily alkylated by halo carboxylic acids and readily acylated by acid chlorides. In the present investigation we have studied the acylation and alkylation of cysteine and 3,3-dimethylcysteine by more complex derivatives of carboxylic acids containing both a halogen and an acylamino group, such as N-acyl-3-haloalanines. Only very few acids of this type are known, and these are prepared by complex transformations of the difficultly accessible serine [2, 3, 4, 5, 6]. In the present communication it is shown that N-acyl-3-haloalanines can be prepared by addition of hydrogen bromide or hydrogen chloride to 2-(acylamino)acrylic acids [7]:

$$CH_2 = \underset{\displaystyle NHCOR}{\overset{\displaystyle |}{C}} - COOH \xrightarrow{HX} CH_2X - \underset{\displaystyle NHCOR}{\overset{\displaystyle |}{CH}} - COOH$$

X = Cl, Br; R = C_6H_5, $CH_2C_6H_5$.

By the action of a solution of hydrogen bromide in glacial acetic acid on 2-(2-phenylacetamido)acrylic acid, 3-bromo-N-(phenylacetyl)alanine, m.p. 163°, was obtained in almost quantitative yield. In the preparation of N-benzoyl-3-bromoalanine considerable difficulties were met on account of the instability of 2-benzamidoacrylic acid. In presence of traces of moisture, arising from the acetic acid or from inadequately dried hydrogen bromide, the benzamido group was split off with formation of benzamide hydrobromide and derivatives of pyruvic acid. By taking all possible precautions we succeeded in obtaining N-benzoyl-3-bromoalanine, m.p. 136-137°, in 66% yield.

Treatment of 2-(2-phenylacetamido)- and 2-benzamido-acrylic acids with hydrogen chloride in dioxane yielded 3-chloro-N-(phenylacetyl)alanine, m.p. 174-175°, and N-benzoyl-3-chloroalanine, m.p. 143-144°, respectively. The last compound has been prepared previously by Fry [5] by the action of hydrogen chloride on 2-phenyl-2-oxazoline-4-carboxylic acid, which was itself prepared by the action of thionyl chloride on an ester of serine.

When treated with diazomethane, 3-bromo-N-(phenylacetyl)alanine is readily converted into its methyl ester, m.p. 87-89°. Treatment of the same compound with aqueous caustic alkali yields 2-(2-phenylacetamido) acrylic acid and the previously unknown O-(phenylacetyl)serine, m.p. 153°.

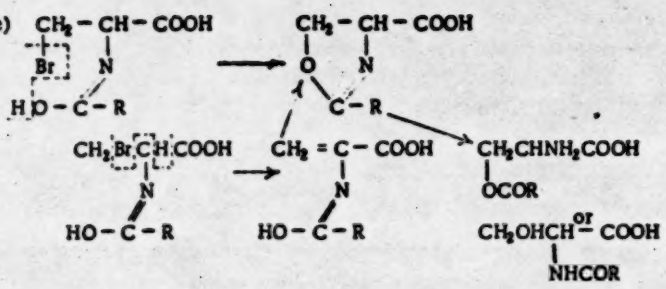
$$BrCH_2CH(NHCOCH_2C_6H_5)-COOH \xrightarrow{NaOH} \begin{cases} \text{2 molecules: } CH_2 = C(NHCOCH_2C_6H_5)-COOH \\ \text{1 molecule: } CH_2(O-COCH_2C_6H_5)-CHNH_2-COOH \end{cases}$$

The formation of an O-acyl derivative of serine is the result of complex transformations.

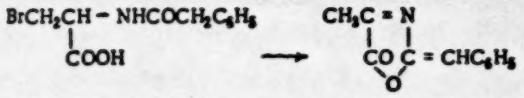
It is probable that at first an unstable oxazoline is formed, either by the elimination of HBr from the enol form of 3-bromo-N-(phenylacetyl)alanine or by elimination of HBr with formation of an acrylic acid derivative followed by addition of the enol hydroxyl at the double bond. Hydrolysis of the oxazoline, depending on the conditions (pH of medium), leads to an N- or O-acyl derivative of serine. (See top of next page).

When 3-bromo-N-(phenylacetyl)alanine was heated with very dilute hydrobromic acid, serine was formed in 78% yield. This appears to be the best method of preparing serine. Under the same conditions N-benzoyl-3-bromoalanine was converted into O-benzoylserine, serine itself being obtained under more severe conditions (heating with 20% hydrochloric acid).

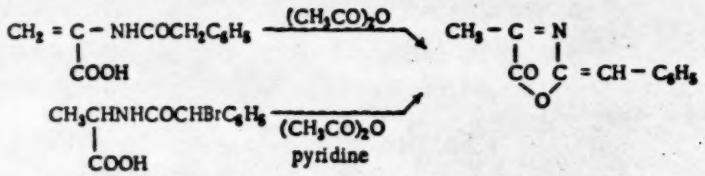
(formula from preceding page)



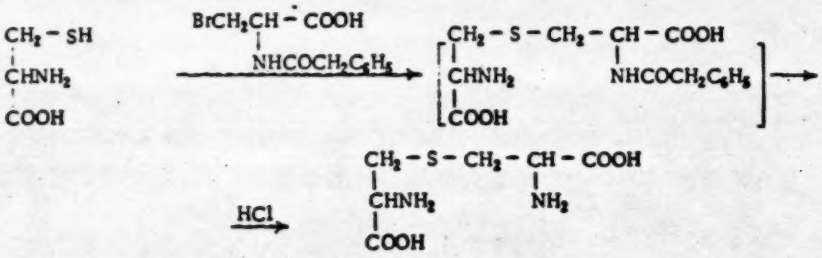
When attempts were made to prepare an acid chloride or mixed anhydride of 3-bromo-N-(phenylacety)-alanine by treatment with PCl_5, $SOCl_2$, or acetic anhydride, the product obtained was always 2-benzylidene-4-methyl-3-oxazolin-5-one, m.p. 129-131°:



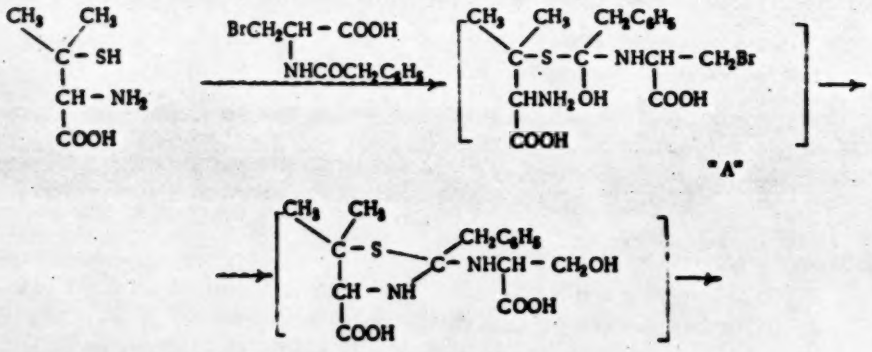
This 3-oxazolin-5-one has been prepared previously by the action of acetic anhydride on 2-(2-phenylacetamido) acrylic acid and by the action of acetic anhydride in presence of pyridine on N-[bromo(phenyl)acetyl]alanine [8]:

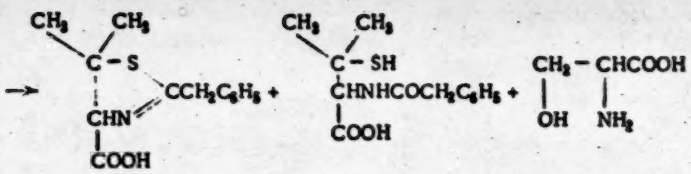


We proceeded to a study of the alkylation of mercapto amino acids with 3-bromo-N-(phenylacetyl) alanine. Reaction of the latter compound with cysteine gave a 50% yield of lanthionine:

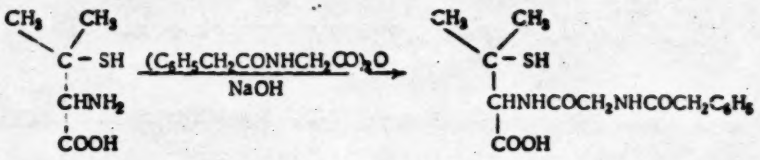


We have thus effected the S-alkylation of cysteine with an acid carrying a residue in the α-position which is present also in penicillin D. However, an attempt to carry out the same reaction with 3,3-dimethyl-cysteine gave unexpected results: instead of the expected S-alkylation, transacylation occurred, probably with intermediate formation of the unstable addition product "A", which undergoes decomposition in several directions under the action of acids. Reaction products isolated were serine, 3,3-dimethyl-N-(phenylacetyl)cysteine, and 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m.p. 140-141°:

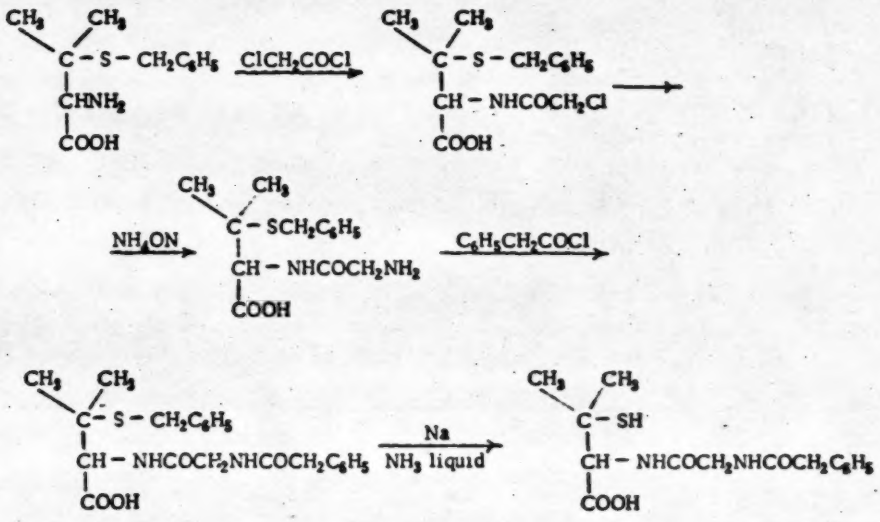




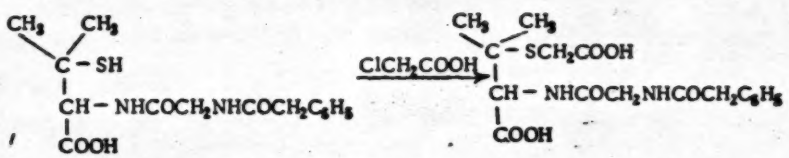
Further investigation showed that 3,3-dimethylcysteine is readily acylated with anhydrides of α-acylamino acids. Thus, under Schotten-Baumann conditions, 3,3-dimethyl-N-phenaceturylcysteine was readily obtained by the action of phenaceturic anhydride on 3,3-dimethylcysteine:



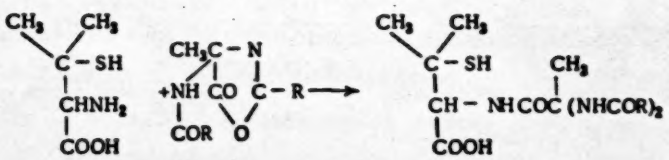
The product was identical with the 3,3-dimethyl-N-phenaceturylcysteine obtained by Sûs [9] by the following sequence of reactions:



Treatment of 3,3-dimethyl-N-phenaceturylcysteine with chloroacetic acid yielded S-(carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine, which decomposed at 90°:



The reactions of 3,3-dimethylcysteine with saturated oxazolinones resulted in the preparation of new N-acylated derivatives of 3,3-dimethylcysteine. Thus, the acylation of 3,3-dimethylcysteine with 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one [10] yielded N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine, m.p. 203-204°. Acylation of 3,3-dimethylcysteine with 2-benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one [11] yielded N-[2,2-bis(2-phenylacetamido)propionyl]-3,3-dimethylcysteine, m.p. 187-189°:



R = C_6H_5 $CH_2C_6H_5$

It was to be expected that this last compound could be converted into an N-[2-(acylamino)acryloyl]-3,3-dimethylcysteine, just as 2,2-bis(acylamino)propionic acids can be converted into 2-(acylamino)acrylic acids. However, we have not yet succeeded in effecting this elimination of amide, neither by heating in glacial acetic acid nor by heating at the melting point, nor by boiling in benzene in presence of pyruvic acid.

EXPERIMENTAL

3-Bromo-N-(phenylacetyl)alanine. 2-(2-Phenylacetamido)acrylic acid (10.5 g, i.e. 0.1 mole) was introduced into 70 ml of glacial acetic acid containing 18 g of hydrogen bromide. After one hour the whole of the acid had dissolved. The solution was set aside at room temperature until the next day, when it was poured into 200 ml of ice water. The resulting precipitate was filtered off, washed with water until there was no longer an acid reaction to Congo red, and dried. The product was 25 g (90%) of 3-bromo-N-(phenylacetyl)alanine, m.p. 163° after recrystallization from ethyl acetate. 3-Bromo-N-(phenylacetyl)alanine is readily soluble in alcohol, acetone, and dioxane, sparingly in ether, benzene, heptane, and chloroform. It is insoluble in cold water, and when it is heated with water HBr is eliminated, the same reaction being effected also by sodium bicarbonate, silver nitrate solution, or pyridine.

	Found%:	C 46.00; H 4.21; N 5.1; Br 28.24
$C_{11}H_{12}O_3NBr$.	Calculated %:	C 46.17; H 4.19; N 4.89; Br 27.93

Methyl Ester of 3-Bromo-N-(phenylacetyl)alanine. 3-Bromo-N-(phenylacetyl)alanine (6.5 g) was treated with an ether solution of diazomethane until decolorization no longer occurred. During the treatment the acid dissolved, and after some time a new precipitate formed; it was filtered off and washed with ether on the filter. The product was 3.4 g of the methyl ester of 3-bromo-N-(phenylacetyl)alanine, m.p. 87-89°. A further 2.1 g of ester was isolated from the mother liquor (total yield 74.7%). The methyl ester of 3-bromo-N- (phenylacetyl)-alanine is readily soluble in alcohol, less readily in ether. It can be recrystallized from water if heating is done cautiously.

	Found %:	C 48.28; H 4.74; Br 26.00; N 4.98
$C_{12}H_{14}O_3NBr$.	Calculated %:	C 48.01; H 4.70; Br 26.66; N 4.67

Acid Hydrolysis of 3-Bromo-N-(phenylacetyl)alanine (Preparation of Serine). A suspension of 50 g of 3-bromo-N-(phenylacetyl)alanine in 300 ml of water containing 1 ml of 40% HBr was heated under reflux; it was first heated on a water bath until the acid dissolved, and was then boiled for three hours. The solution was cooled, and the precipitated phenylacetic acid was filtered off; the filtrate was extracted three times with ether to remove phenylacetic acid completely. The aqueous solution was evaporated to dryness under reduced pressure. The residue was dissolved in 60 ml of 80% ethanol, and concentrated aqueous ammonia was added, with cooling, until the odor persisted. The mixture was left overnight in a refrigerator, and on the next day the precipitate was filtered off, washed with absolute alcohol, and dried. The product was 17 g of serine, m.p. 180 – 190°. Recrystallization from water yielded 13.1 g of serine, m.p. 230° (dec.). By addition of alcohol to the mother liquor, a further 1.4 g of serine was obtained. The total yield was 78.5%.

	Found %:	C 33.51; H 6.59; N 13.47
$C_3H_7O_3N$.	Calculated %:	C 34.28; H 6.71; N 13.39

The serine that we prepared was identified by means of chromatography on paper with serine prepared by another method. The hydrochloride of the methyl ester of serine and 3-chloroalanine were prepared from the serine and found to have melting points identical with those reported in the literature [3].

2-Benzylidene-4-methyl-3-oxazolin-5-one. A mixture of 0.8 g of 3-bromo-N-(phenylacetyl)alanine and 6 ml of acetic anhydride was warmed carefully until the acid dissolved, and acetic anhydride was then distilled off rapidly under reduced pressure. The residue was treated several times with absolute ether. The ether extract was filtered, and the ether was removed under reduced pressure. The residue was recrystallized from methanol and yielded 2-benzylidene-4-methyl-3-oxazolin-5-one in the form of light-yellow crystals melting at 129-131° [8]. The substance has an irritating effect on the eyes and mucous membrane.

S-Alkylation of Cysteine with 3-Bromo-N-(phenylacetyl)alanine. To a solution of 0.12 g (0.001 mole) of cysteine in 2 ml of NaOH (0.002 mole), 0.26 g (0.001 mole) of 3-bromo-N-(phenylacetyl)alanine was added. The solution was maintained alkaline by dropwise addition of 1 ml of N NaOH, and the mixture was set aside at room temperature overnight. On the next day the solution was evaporated to dryness at 50-60° under reduced pressure, and 4 ml of 20% hydrochloric acid was added to the residue. The mixture was refluxed for three hours, and the precipitated phenylacetic acid was filtered off. The filtrate was extracted three times with ether to remove residual phenylacetic acid. The aqueous solution was evaporated to dryness under reduced pressure, and the residue was dissolved in 1 ml of water. Saturated sodium acetate solution (1 ml) was added, and the

precipitate formed was filtered off. The product was 0.1 g (50%) of lanthionine, melting with decomposition at 240°.

The lanthionine was purified for the analysis by reprecipitation from hydrochloric acid solution with saturated sodium acetate solution.

	Found %:	C 33.27; H 5.98; S 14.84
$C_6H_{12}O_4N_2S$.	Calculated %:	C 34.60; H 5.8; S 15.40

The substance was identical in properties with a sample of lanthionine specially prepared by Schoberl's method [12].

Reaction of 3,3-Dimethylcysteine with 3-Bromo-N-(phenylacetyl)alanine. To a solution of 0.6 g (0.004 mole) of 3,3-dimethylcysteine in 8 ml of N NaOH (0.008 mole), 1.15 g (0.004 mole) of 3-bromo-N-(phenylacetyl)-alanine was added. The solution was maintained alkaline by gradual addition of N NaOH (2 ml). The reaction mixture was set aside at room temperature overnight. On the next day there was still a feeble reaction for the mercapto group. The solution was acidified to pH 3.5-4 with 2 N HCl, and the oil formed was separated. When this oil was treated with 2 N HCl, part of it dissolved, and addition of a saturated sodium bicarbonate solution to the resulting solution until the pH was 3.5-4 yielded 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m.p. 141-143°.

	Found %:	C 62.44; H 6.16; S 12.56; N 5.5
$C_{13}H_{15}O_2NS$.	Calculated %:	C 62.62; H 6.06; S 12.86; N 5.62

The residue, insoluble in hydrochloric acid, was recrystallized from water. The product was 3,3-dimethyl-N-(phenylacetyl)cysteine, m.p. 129-130°, undepressed by admixture of known 3,3-dimethyl-N-(phenylacetyl)-cysteine.

The solution remaining after separation of the oil was evaporated to dryness under reduced pressure, and the residue was dissolved in absolute alcohol. Ammonia was added to the alcoholic solution until the odor persisted, and the mixture was set aside in a refrigerator overnight. The precipitate formed was recrystallized from water, and it then melted with decomposition at 220°. It gave a positive ninhydrin test for α-amino acids; it did not contain sulfur; it had a sweet taste. In admixture with serine it showed no melting point depression.

N-Benzoyl-3-bromoalanine. Dry hydrogen bromide (dried over phosphoric oxide) was passed into a suspension of 2 g (0.01 mole) of 2-benzamidoacrylic acid in 4 ml of glacial acetic acid (distilled over phosphoric oxide). After ten minutes the whole of the acid had dissolved. When HBr ceased to be absorbed (one hour), the solution was poured into 12 ml of ice water. The oil that separated solidified and it was filtered off and washed with cold water until it ceased to be acid to Congo red. The product was 1.9 g (66%) of N-benzoyl-3-bromoalanine, which melted with decomposition at 136-137° after recrystallization from ethyl acetate. The acid is readily soluble in alcohol and acetone, and it can be recrystallized from ether. An exactly weighed sample of the acid was boiled with 0.1 N NaOH for 20 minutes, and the solution was acidified with nitric acid and titrated by Volhard's method.

	Found %:	Br 29.2
$C_{10}H_{10}O_3NBr$.	Calculated %:	Br 29.4

With diazomethane N-benzoyl-3-bromoalanine yielded its methyl ester, m.p. 116-117° (the literature [6] gives 115-117°).

O-Benzoylserine. A mixture of 2.7 g of N-benzoyl-3-bromoalanine, 15 ml of water, and 2-3 drops of 40% HCl was heated under reflux until the acid dissolved, and then boiled for two hours. The solution was evaporated to one-fifth bulk under reduced pressure, and was extracted with ether. Concentrated ammonia was added to the aqueous solution until the odor persisted, and the mixture was set aside in a refrigerator for four hours. The finely crystalline precipitate was filtered off. The product was O-benzoylserine, m.p. 150°; the O-benzoylserine prepared by Fry [5] by the hydrolysis of 2-phenyl-2-oxazoline-4-carboxylic acid also melted at 150°. O-Benzoylserine gives a positive ninhydrin test for α-amino acid. A further 0.5 g of O-benzoylserine was obtained from the mother liquor. The total yield was 75%.

	Found %:	C 57.07; H 4.99
$C_{10}H_{11}O_4N$.	Calculated %:	C 57.41; H 5.30

In order to obtain serine, N-benzoyl-3-bromoalanine must be boiled for two hours with 20% hydrochloric acid.

N-Benzoyl-3-chloroalanine*. Dry hydrogen chloride was passed for one hour into a solution of 5 g of 2-benzamidoacrylic acid in 25 ml of dry dioxane. Dioxane was removed under reduced pressure, and 10 ml of ice water was added to the residue. The precipitate was filtered off, washed with ice water until no longer acid to Congo red, and dried. The product was 3.3 g of N-benzoyl-3-chloroalanine, m.p. 143-144° (after being washed with warm benzene and chloroform). Fry [6] gives a value of 145-147° for the melting point of N-benzoyl-3-chloroalanine.

Found %: C 53.41; H 4.52; Cl 14.26
$C_{10}H_{10}O_3NCl$. Calculated %: C 52.76; H 4.43; Cl 15.58

3-Chloro-N-(phenylacetyl)alanine*. Treatment of 2-(2-phenylacetamido)acrylic acid by the same method yielded 3-chloro-N-(phenylacetyl)alanine, m.p. 174-175° (from ethyl acetate).

Found %: C 54.43; H 5.15; Cl 14.73
$C_{11}H_{12}O_3NCl$. Calculated %: C 54.66; H 5.01; Cl 14.67

Phenaceturic Anhydride. A mixture of 10 g of phenaceturic acid and 30 ml of acetic anhydride was heated for 5-10 minutes at 60° at a residual pressure of 40 mm; the whole of the acid dissolved. The temperature was lowered to 30-40° and acetic anhydride was distilled off under reduced pressure until crystallization began. The crystals were filtered off, washed with ether, with sodium bicarbonate solution, and with water, and dried over phosphoric oxide in a desiccator. The product was 6 g (64.5%) of phenaceturic anhydride, m.p. 115-117°. Strukov has prepared phenaceturic anhydride, for which he gives the melting point 108-109° [13].

3,3-Dimethyl-N-phenaceturylcysteine. Phenaceturic anhydride (1.84 g, i.e. 0.005 mole) was added at 10° to 0.73 g (0.005 mole) of 3,3-dimethylcysteine in 5 ml of water containing 0.4 g (0.01 mole) of sodium hydroxide, and the mixture was shaken until the anhydride dissolved (5-10 minutes). The solution was acidified to Congo red with 2 N HCl, and the precipitate that formed, which consisted of a mixture of 3,3-dimethyl-N-phenaceturylcysteine and phenaceturic acid, was repeatedly crystallized from hot water (the temperature of the water was not above 70°). The product was 0.8 g (50%) of 3,3-dimethyl-N-phenaceturylcysteine, m.p. 142-144°.

Found %: C 55.63; H 6.19; S 9.95
$C_{15}H_{20}O_4N_2S$. Calculated %: C 55.53; H 6.21; S 9.88

S-(Carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine. Chloroacetic acid (0.4 g, i.e. 0.004 mole) was added at 0° to 0.65 g (0.002 mole) of 3,3-dimethyl-N-phenaceturylcysteine in 2 ml of 2 N NaOH, and 2 N NaOH was added until the mixture was alkaline to phenolphthalein. After one hour positive tests for the SH group were no longer obtained. The solution was cooled with ice and acidified to Congo red with concentrated hydrochloric acid. The oil that separated solidified when rubbed out with ether. After purification by reprecipitation with ether from alcoholic solution, the S-(carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine melted at 99-100° with decomposition.

Found %: C 53.65; H 5.97; N 7.66
$C_{17}H_{22}O_6N_2S$. Calculated %: C 53.38; H 5.80; N 7.32

4-Benzamido-4-methyl-2-phenyl-2-oxazolin-5-one. This substance was prepared by Nicolet's method [10] by the action of acetic anhydride on 2,2-dibenzamidopropionic acid. After being recrystallized from benzene it melted at 193°.

Methyl 2,2-Dibenzamidopropionate. Treatment of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one with methanol containing traces of HCl resulted in the formation of methyl 2,2-dibenzamidopropionate, m.p. 167-168°. A mixture test with the ester obtained by treating 2,2-dibenzamidopropionic acid with diazomethane showed no depression.

Hydrochloride of 4-Benzamido-4-methyl-2-phenyl-2-oxazolin-5-one. Freshly distilled thionyl chloride (3 g) was poured onto 1.5 g of 2,2-dibenzamidopropionic acid. In the course of 30 minutes the whole of the acid dissolved and a new crystalline precipitate formed. The reaction mixture was heated under reflux in a water bath until bubbles of gas ceased to be evolved. Excess of thionyl chloride was removed under reduced pressure. The residue was washed with absolute ether. The product was 1.4 g of the hydrochloride of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one, melting with decomposition at 160°. An exactly weighed sample of the oxazolinone hydrochloride was shaken with water, nitric acid was added, and ionic chlorine was titrated by Volhard.

* A. I. Guseva aided in the preparation of N-benzoyl-3-chloro- and 3-chloro-N-(phenylacetyl)-alanines.

Found %: Cl 10.60

$C_{17}H_{15}O_3N_2Cl$. Calculated %: Cl 10.72

When the oxazolinone hydrochloride was boiled with 2 molecular proportions of 0.1 N NaOH and the solution acidified, the original 2,2-dibenzamidopropionic acid was recovered.

N-(2,2-Dibenzamidopropionyl)-3,3-dimethylcysteine. To a solution of 0.5 g (0.0033 mole) of 3,3-dimethylcysteine in 13 ml of 0.5 N NaOH (0.0066 mole) 1 g (0.0033 mole) of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one was added. The reaction mixture was maintained at 50° for three hours, in the course of which almost the whole of the oxazolinone went into solution. The solution was filtered and acidified to Congo red with N HCl. The precipitate that formed was filtered off, washed with water, and dried. The product was 0.75 g (50%) of N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine, m.p. 203-208°. The substance was purified by reprecipitation from alcoholic solution with water.

Found %: C 59.30; H 5.54; S 6.86

$C_{22}H_{25}O_5N_3S$. Calculated %: C 59.57; H 5.68; S 7.23

N-(2,2-Dibenzamidopropionyl)-3,3-dimethylcysteine is readily soluble in ethyl, methyl, and butyl alcohols, and in chloroform, ethyl acetate, and dioxane; it is insoluble in water and ether.

2-Benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one (Oxazolinone derived from 2,2-Bis(2-phenylacetamido)propionic Acid). A mixture of 3.4 g (0.1 mole) of 2,2-bis (2-phenylacetamido)propionic acid and 12 ml of acetic anhydride was heated in a water bath until the acid had completely dissolved (two hours). The mixture was then cooled to room temperature and practically the whole of it solidified. The precipitate was filtered off, washed with sodium bicarbonate solution and with water, and dried. The product was 2.3 g (70%) of the oxazolinone, m.p. 169-170° (from absolute ethyl acetate).

Found %: C 71.21; H 5.76

$C_{19}H_{18}O_3N_2$. Calculated %: C 70.79; H 5.35

N-[2,2-Bis(2-phenylacetamido)propionyl]-3,3-dimethylcysteine. 2-Benzyl-4-methy-4-(2-phenylacetamido)-2-oxazolin-5-one (0.65 g, i.e. 0.002 mole) was added to 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 4 ml of N NaOH (0.004 mole), and the mixture was maintained at 50° until the oxazolinone had dissolved completely (30 minutes). The solution was filtered and acidified to Congo red with N HCl. The precipitate formed was filtered off, washed with water, and dried. The product was 0.37 g (30%) of N-[2,2-bis(2-phenylacetamido)-propionyl]-3,3-dimethylcysteine, melting at 187-189° after three crystallizations form 50% alcohol.

Found %: C 61.25; H 5.8; S 6.58

$C_{24}H_{29}O_5N_3S$. Calculated %: C 61.12; H 5.[illegible]; S 6.80

SUMMARY

1. α-Acylamino β-halo acids were prepared by addition of hydrogen bromide and hydrogen chloride to 2-(acylamino)acrylic acids. Serine was prepared in almost quantitative yield by the hydrolysis of 3-bromo-N-(phenylacetyl)alanine.

2. It was shown that 3,3-dimethylcysteine is readily acylated under normal conditions by oxazolinones and anhydrides of acylamino carboxylic acids with formation of N-acyl derivatives, for example, 3,3-dimethyl-N-phenaceturylcysteine and N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine.

3. The reaction of 3,3-dimethylcysteine with 3-bromo-N-(phenylacetyl)alanine in aqueous medium is accompanied by intermolecular transacylation with formation of 3,3-dimethyl-N-(phenylacetyl)cysteine and 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid.

LITERATURE CITED

[1] I. L. Knunyants and M. G. Linkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 62. •

[2] E. Rotstein, J. Chem. Soc. 1949, 1968.

[3] E. P. Pointer, J. Am. Chem. Soc., 69, 229 (1947).

• Consultant's Bureau Translation. p 53.

[4] M. Bergmann, K. Grafe, Z. physiol. Chem. 187, 197 (1930).

[5] E. Fry, J. org. Chem. 14, 887 (1949).

[6] E. Fry J. org. Chem. 15, 438 (1950).

[7] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 271.*

[8] Chemistry of Penicillin, Princeton Univ. Press, 1949, 794, 798.

[9] O. Süs, Ann. 561, 31 (1948).

[10] B. Nicolet, J. Am. Chem. Soc. 57, 1073 (1935).

[11] M. Brenner, K. Rüfenacht, Helv. 36, 1832 (1953).

[12] A. Schoberl, A. Wagner, Ber. 80, 379 (1947).

[13] I. T. Strukov, J. Gen. Chem. 23, 438 (1953).**

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

---

* Consultant's Bureau Translation, p 241

** Consultant's Bureau Translation, p 449

NEW METHOD FOR THE PREPARATION OF PRIMARY AND SECONDARY ORGANOARSENIC COMPOUNDS

I. L. Knunyants and V. Ya. Pilskaya

Among the numerous methods for the preparation of organoarsenic compounds, the most important are those yielding alkyl- and aryl-arsonic acids. The most noteworthy of these methods are those due to Meyer [1] and to Burt [2]. From the preparative point of view, Meyer's method has been found very convenient for various alkylarsonic acids, but some of these arsonic acids are obtained in very low yield, the yields of butyl- and isopentyl arsonic acids, for example, being only 5–10%.[3].

The yield obtained in Meyer s reaction depends on the reactivity of the alkyl halide. Whereas benzyl and allyl bromide, and 2-chloroethanol react with an arsenite at a high rate, ethyl bromide, and particularly isopropyl bromide, phenoxypropyl bromide, and ethylene dibromide, react very slowly with sodium arsenite, and practically no arsonic acid is formed [3]. Phenethyl bromide does not react with sodium arsenite, neither under the usual conditions, nor at 180° in presence of copper [4], and styryl bromide, in reacting with sodium arsenite, forms styrylarsonic acid in only very low yield.

It is known that aryl halides react with alkali-metal arsenites only under special conditions. The same applies to halogen derivatives of thiophene and furan [5]. Secondary alkyl halides react with difficulty with arsenic trioxide, and the tertiary do not react at all [6].

Meyer's reaction, therefore, in spite of its simplicity and of the accessibility of the starting materials, has some limitations that restrict its applicability.

The present investigation is devoted to the development of a method for the preparation of organoarsenic compounds which will be convenient for the preparation of some difficultly accessible compounds. The method consists in the preparation of alkyl- and aryl-(2-chlorovinyl)arsines, followed by elimination of the 2-chlorovinyl group. The possibility of such elimination is based on the tendency of 2-chlorovinylarsenic compounds to undergo cleavage under the action of alkalis. Such compounds include, in particular, dichloro(2-chlorovinyl)arsine and chlorobis(2-chlorovinyl)arsine.

It is known that the stereoisomeric dichloro(2-chlorovinyl)arsines behave differently toward alkalis. Whereas the trans isomer yields acetylene quantitatively when treated with a 15% solution of caustic alkali in the cold, cis-dichloro(2-chlorovinyl)arsine, treated in a similar way, yields only disodium 2-chlorovinyl arsenite, which will then give vinyl chloride when heated with alkali to 40-80° [7]. Dichloro-(2-chlorovinyl)- and chlorobis(2-chlorovinyl)-arsines, being acid chlorides containing very mobile chlorine atoms, readily react with organomagnesium compounds, and as a result alkyl- and aryl-bis(2-chlorovinyl)arsines and dialkyl- and diaryl-(2-chlorovinyl)arsines are obtained [8, 9]. The resulting tertiary alkyl- and aryl-(2-chlorovinyl)arsines should retain the characteristic properties of 2-chlorovinyl compounds. Since there is about 90% of the trans form in technical dichloro(2-chlorovinyl)arsine [7], the trans configuration of the 2-chlorovinyl group should predominate also in tertiary alkyl- and aryl-(2-chlorovinyl)arsines obtained from lewisite and confer the characteristic property of acetylene evolution under the action of alkaline reagents.

The method that we have developed consists essentially in the reaction of alkylmagnesium halide with chlorobis(2-chlorovinyl)arsine or dichloro(2-chlorovinyl)arsine to yield tertiary arsines:

$$RMgX + ClAs(CH{=}CHCl)_2 \rightarrow RAs(CH{=}CHCl)_2 + MgXCl$$

or

$$2RMgX + Cl_2AsCH{=}CHCl \rightarrow R_2AsCH{=}CHCl + 2MgXCl$$

The resulting tertiary (2-chlorovinyl)arsine is decomposed with aqueous or alcoholic alkali:

$$RAs(CH{=}CHCl)_2 + 2NaOH \rightarrow RAsO + 2C_2H_2 + 2NaCl + H_2O$$

or

$$2R_2AsCH{=}CHCl + 2NaOH \rightarrow [R_2As]_2O + 2C_2H_2 + 2NaCl + H_2O.$$

This method was verified for methyl iodide, ethyl bromide, propyl bromide, isopropyl bromide, butyl bromide, butyl iodide, isopentyl bromide, bromobenzene, p-bromotoluene, cyclohexyl bromide, and styryl bromide.

These alkyl halides were treated with magnesium in dry ether in order to obtain the corresponding alkylmagnesium halides which were then caused to react with chlorobis(2-chlorovinyl)arsine, when they yielded a series of alkyl- and aryl-bis(2-chlorovinyl)arsines (Table 1).

TABLE 1

Alkyl or aryl halide	Tertiary arsine	B.p. in °C (p in mm)	Yield (%)
CH_3I	$CH_3As(CH = CHCl)_2$	142 (10)	
C_2H_5Br	$C_2H_5As(CH = CHCl)_2$	100 (6)	
$n\text{-}C_3H_7Br$	$n\text{-}C_3H_7As(CH = CHCl)_2$*	112 (4)	89.4
$i\text{-}C_3H_7Br$	$i\text{-}C_3H_7As(CH = CHCl)_2$*	115 (10)	79.8
$n\text{-}C_4H_9Br$	$n\text{-}C_4H_9As\ CH = CHCl)_2$*	106 (8)	89.3
$i\text{-}C_5H_{11}Br$	$i\text{-}C_5H_{11}As(CH = CHCl)_2$*	126 (3)	87.5
C_6H_5Br	$C_6H_5As(CH = CHCl)_2$	170 (5)	
$p\text{-}CH_3C_6H_4Br$	$p\text{-}CH_3C_6H_4As(CH = CHCl)_2$*	165 (3)	78.3
$cyclo\text{-}C_6H_{11}Br$	$cyclo\text{-}C_6H_{11}As(CH = CHCl)_2$*	148 (10)	73.3
$C_6H_5CH = CHBr$	$C_6H_5CH = CHAs(CH = CHCl)_2$*	125 (3)	44

* Compounds not described previously.

Reaction of alkylmagnesium halides with dichloro(2-chlorovinyl)arsine yielded the tertiary arsines listed in Table 2.

TABLE 2

Alkyl or aryl halide	Tertiary arsine	B.p. in°C (p in mm)	Yield (%)
CH_3I	$(CH_3)_2As - CH = CHCl$*	42 (13)	51
C_2H_5Br	$(C_2H_5)_2AsCH = CHCl$*	66 (7)	69.6
$i\text{-}C_3H_7Br$	$(i\text{-}C_3H_7)_2As - CH = CHCl$*	90 (6)	47
$n\text{-}C_4H_9Br$	$(n\text{-}C_4H_9)_2As - CH = CHCl$*	110 (3)	67
$i\text{-}C_5H_{11}Br$	$(i\text{-}C_5H_{11})_2As - CH = CHCl$*	123 (3)	66.5
C_6H_5Br	$(C_6H_5)_2As - CH = CHCl$*	176 (3)	57
$n\text{-}CH_3C_6H_4Br$	$(n\text{-}CH_3C_6H_4)_2As - CH = CHCl$*	197 (3)	59.5

* Compounds not described previously

In these reactions tertiary arsines are formed in high yields. It must be pointed out that, in the decomposition of alkyl- and aryl-(2-chlorovinyl)arsines, the yield of acetylene is not 100%. The fact that acetylene is eliminated in an amount approximating to 90% of the theoretical yield indicates that about 90% of the tertiary arsine has 2-chlorovinyl groups in the trans configuration. The conversion of the organoarsenic oxides, formed as a result of the alkaline decomposition of alkyl(2-chlorovinyl)arsines, into haloarsines presents no difficulty.

TABLE 3

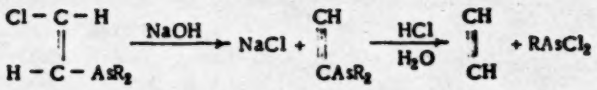
Haloarsine	Yield (%)		
	Meyer's method	Cleavage of 10-alkyl-5,10 dihydrophenarsazine with hydrochloric acid.	Proposed method
CH_3AsCl_2	78*	67	64.4
$C_2H_5AsCl_2$	77*	65	57.2
$n\text{-}C_3H_7AsCl_2$	65*	64	74.1
$i\text{-}C_3H_7AsCl_2$	0	67	58.1
$n\text{-}C_4H_9AsCl_2$	10*	52	84.9
$i\text{-}C_5H_{11}AsCl_2$	5-10*	51	74.6
$C_6H_5AsCl_2$	–		79.4
$p\text{-}CH_3C_6H_4AsCl_2$	–		92.2
$C_6H_5CH{=}CHAsCl_2$	0		41.8
$(CH_3)_2AsCl$		–	59.2
$(C_6H_5)_2AsCl$		–	52.8
$(i\text{-}C_5H_{11})_2AsCl$	0	–	44.4

Table 3 gives the yields of the corresponding haloarsines, as prepared by Meyer's method, by the cleavage of 10-alkyl-5, 10-dihydrophenarsazine with hydrochloric acid (Zeide's method), and by the new method that we have proposed.

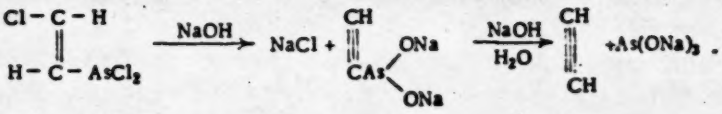
* This column gives the yield of arsonic acid, not haloarsine.

/An analysis of the data in Table 3 shows that the proposed method has advantages over Meyer's method in the preparations of dichloroisopropylarsine, butyldichloroarsine, dichloroisopentylarsine, dichlorostyrylarsine, and chlorodiisopentylarsine. The proposed method has preparative advantages over Zeide's method, and in addition it makes it possible to prepare secondary organoarsenic oxides also.

An unequivocal interpretation of the mechanism of the decomposition of 2-chlorovinyl organometallic compounds has not yet been given [11, 12]. The most probable scheme for the decomposition is elimination of HCl from alkyl(2-chlorovinyl)arsines with formation of alkylethynylarsines, and the decomposition of these by water or hydrochloric acid to yield acetylene and the corresponding haloarsine (or organoarsenic oxide):



It must be supposed that the cleavage of trans-dichloro(2-chlorovinyl)arsine (α-lewisite) will proceed according to a similar scheme:



Indirect confirmation of the formation of alkylethynylarsines is provided by experiments that we have carried out on the decomposition of the above-mentioned tertiary arsines with sodium ethoxide and with amines at room temperature. As objects for investigation (2-chlorovinyl)diethylarsine and dibutyl(2-chlorovinyl)arsine were taken. When dibutyl(2-chlorovinyl)arsine was treated with piperidine for four hours at room temperature, 20% of the theoretical amount of piperidine hydrochloride was isolated, and in the decomposition of (2-chlorovinyl) diethylarsine with alcoholic alkali 24.9% of the theoretical amount of sodium chloride was obtained; in both experiments the yield of acetylene was only 1%. The noncorrespondence between the amount of piperidine hydrochloride or sodium chloride isolated and the amount of acetylene obtained may be regarded as evidence of the formation of alkylethynylarsines.

EXPERIMENTAL

Preparation of Starting Materials. Tertiary alkyl- and aryl-arsines of the type $RAs(CH = CHCl)_2$ were prepared from the corresponding alkyl- and aryl-magnesium halides and freshly distilled chlorobis(2-chlorovinyl)arsine, b.p. 101-102° (3 mm); d_4^{20} 1.7018; n_D^{20} 1.6088. Tertiary arsines of the type $R_2AsCH = CHCl$ were prepared from freshly distilled dichloro(2-chlorovinyl)arsine, b.p. 71-72° (3 mm); d_4^{20} 1.8879; n_D^{20} 1.6108.

1. Preparation of Bis(2-chlorovinyl)propylarsine. A solution of 47 g of chlorobis(2-chlorovinyl)arsine in 250 ml of dry ether was added dropwise with vigorous stirring and ice-cooling to a Grignard reagent prepared from 8 g of magnesium turnings and 43 g of propyl iodide in 100 ml of dry ether. The reaction mixture was then heated in a water bath for one hour. It was then cooled and poured carefully into ice water containing some hydrochloric acid. The ether layer was separated and washed three times with ice water; the aqueous layer was extracted with ether. The ether extracts were united and dried with sodium sulfate. The ether was distilled off, and the oil that remained was vacuum-distilled, when it yielded a clear colorless liquid, b.p. 112° (4 mm); d_4^{20} 1.4174; n_D^{20} 1.5522; yield 43 g (89%).

	Found %:	Cl 29.33; As 30.84
$C_7H_{11}Cl_2As$	Calculated %:	Cl 29.43; As 31.11

2. Conversion of Bis(2-chlorovinyl)propylarsine into Dichloropropylarsine. Dry caustic potash powder (13 g) and ethanol (100 ml) were placed in a round-bottomed flask fitted with reflux condenser connected to a calibrated gas holder. Bis(2-chlorovinyl)propylarsine (b.p. 112°/4 mm) (24 g) was added gradually from a dropping funnel. When acetylene ceased to be evolved (3.5 liters, i.e. 78% of the theoretical amount, was obtained), alcohol was distilled from the reaction mixture, and dichloropropylarsine was isolated from the dry residue. For this purpose excess of hydrochloric acid was added carefully to the dry residue, and the mixture was refluxed in a stream of hydrogen chloride for one hour. The oil that separated was extracted with chloroform, the chloroform solution was dried with sodium sulfate, the chloroform was distilled off, and the oil that remained was vacuum-distilled.

The distillation yielded 14 g (74.1%) of a clear colorless liquid having a sharp unpleasant odor; b.p. 90-93° (46-52 mm); d_{20}^{20} 1.5123; n_D^{20} 1.5358.

3. Bis(2-chlorovinyl)isopropylarsine. This substance was prepared under the conditions of Expt. No. 1 from 8 g of magnesium, 49.7 g of isopropyl bromide, 100 ml of ether and 58 g of chlorobis(2-chlorovinyl)arsine. The substance boiled at 115° (10 mm). The yield was 80%.

	Found %:	Cl 29.39; As 30.89
$C_7H_{11}Cl_2As$	Calculated %:	Cl 29.43; As 31.11

4. Dichloroisopropylarsine from Bis(2-chlorovinyl)isopropylarsine. The preparation was carried out under the conditions of Expt. No. 2 from 15 g of caustic potash, 100 ml of ethanol, and 24 g of bis(2-chlorovinyl)-isopropylarsine. Boiling with hydrochloric acid was for one hour. The product had b.p. 64-66° (12-13 mm); d_4^{20} 1.5722; n_D^{20} 1.5289; The yield was 58%.

5. Butylbis(2-chlorovinyl)arsine. This substance was prepared under the conditions of Expt. No. 1 from 17 g of magnesium, 126 g of butyl iodide, 100 ml of ether, and 116.7 g of chlorobis(2-chlorovinyl)arsine in 250 ml of ether. The product, butylbis(2-chlorovinyl)arsine, had b.p. 105-106° (8 mm); d_4^{20} 1.3660; n_D^{20} 1.5488. The yield was 89.3%.

	Found %:	Cl 27.77; 27.61
$C_8H_{13}Cl_2As$	Calculated %:	Cl 27.81

6. Butyldichloroarsine. Butylbis(2-chlorovinyl)arsine (12.8 g) was decomposed in the usual way with alcoholic alkali, and 2 liters (92% of the theoretical amount) of acetylene was collected. Alcohol was distilled off, and excess of hydrochloric acid was added to the dry residue. The mixture wasrefluxed in a stream of hydrogen chloride for one hour. The oil that separated was extracted with chloroform. Chloroform was distilled off, and vacuum distillation of the oil yielded 8.6 g (89.9%) of a colorless liquid, b.p. 58-60° (5 mm), n_D^{20} 1.5238. Oxidation of a 0.5-g sample of the butyldichloroarsine with hydrogen peroxide yielded 0.4 g (89.2%) of butylarsonic acid, m.p. 158-159°, in the form of white crystals.

7. Bis(2-chlorovinyl)isopentylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 76 g of isopentyl bromide in 100 ml of dry ether, and 58 g of chlorobis(2-chlorovinyl)-arsine in 200 ml of ether. Bis(2-chlorovinyl)isopentylarsine is a clear colorless liquid, b.p. 125-126° (3 mm); d_4^{20} 1.2859; n_D^{20} 1.5390; The yield was 87.5%.

	Found %:	Cl 26.36; As 27.94
$C_9H_{15}ClAs$	Calculated %:	Cl 26.39; As 27.88

8. Dichloroisopentylarsine from Bis (2-chlorovinyl)isopentylarsine. Bis (2-chlorovinyl)isopentylarsine (26 g) was added dropwise to 14 g of caustic potash powder in 100 ml of ethanol. The reaction mixture was heated in a water bath, and the gas evolved was collected in a graduated gas holder (4.2 liters, i.e. 94% of the theoretical amount of gas was collected). From 50 ml of the gas the Ilosvay reagent absorbed 44 ml, corresponding to an acetylene content of 99%. Alcohol was distilled from the reaction mixture, excess of hydrochloric acid was added carefully to the dry residue, and the mixture was heated under reflux in a stream of hydrogen chloride for one hour. The oil that separated was filtered from the precipitate and extracted with chloroform. The chloroform solution was dried with calcium chloride, and the residue after removal of chloroform was vacuum-distilled, when it yielded:

Frac. I, b.p. 91-92° (8 mm); 16.2g

Frac. II, b.p.100-130° (8 mm); 2.9 g (unchanged β-lewisite)

Fraction I, obtained in 74.6% yield, was a clear colorless liquid having a characteristic odor; d_4^{20} 1.3863; n_D^{20} 1.5170 . Oxidation of 1 g of the dichloroisopentylarsine with nitric acid yielded 0.5 g of isopentylarsonic acid in the form of scales melting at 194°.

9. Bis(2-chlorovinyl)-p-tolylarsine. This substance was prepared under the conditions of Expt. No. 1 from 9.6 g of magnesium, 42.7 g of p-bromotoluene, 150 ml of ether, and 49.6 g of chlorobis(2-chlorovinyl)-arsine in 200 ml of dry ether. Bis(2-chlorovinyl)-p-tolylarsine is a clear colorless liquid, b.p. 165-167° (3 mm); d_4^{20} 1.3676; n_D^{20} 1.5990. The yield was 78.3%.

	Found %:	Cl 24.97; As 25.71
$C_{11}H_{11}Cl_2As$	Calculated %:	Cl 24.55; As 25.95

10. Dichloro-p-tolylarsine from Bis(2-chlorovinyl)-p-tolylarsine. Bis(2-chlorovinyl)-p-tolylarsine (20g) was decomposed by heating it with alcoholic caustic potash, when 2.8 liters (90%) of gas was evolved. Alcohol was distilled off, hydrochloric acid (excess) was added cautiously to the dry residue, and the mixture was boiled under reflux in a stream of hydrogen chloride. The oil that separated was extracted with chloroform, and the extract was dried with calcium chloride. After removal of chloroform, 15.1 g (92.7%) of slightly yellowish crystals remained. The melting point of the crude product was 36-37°, and after crystallization from alcohol it melted at 42-43°. Oxidation of 1 g of the product (dichloro-p-tolylarsine) with hydrogen peroxide yielded 0.9 g (98.7%) of p-tolylarsonic acid, m.p. 206.5-207.5°.

11. Bis(2-chlorovinyl)styrylarsine. A Grignard reagent was prepared in the usual way from 6 g of magnesium turnings and 45.6 g of styryl bromide (β-bromostyrene), b.p. 119-122° (35 mm), in 100 ml of dry ether. With vigorous stirring and cooling a solution of 38.9 g of chlorobis(2-chlorovinyl)arsine in 200 ml of dry ether was added dropwise. When the whole of the β-lewisite had been added, the reaction mixture was heated, then set aside overnight, and finally heated again for eight hours. The mixture was poured cautiously into a beaker of ice water to which a little hydrochloric acid had been added. The ether layer was washed three times with cold water, and the aqueous layer was extracted with ether. The ether extracts were united and dried with calcium chloride. The ether was distilled off, and vacuum distillation of the residue yielded 22 g (44%) of a clear colorless liquid, b.p. 125-135° (3 mm) and d_4^{20} 1.4183.

	Found %:	Cl 23.84; As 24.85
$C_{12}H_{11}Cl_2As$.	Calculated %:	Cl 23.67; As 24.91

12. Dichlorostyrylarsine. Bis(2-chlorovinyl)styrylarsine (20 g) was decomposed in the usual way with alcoholic alkali. In the course of the decomposition, 2.9 liters (90%) of acetylene was evolved. Alcohol was distilled off, excess of hydrochloric acid was added to the dry residue, and the mixture was refluxed for one hour. The oil that separated was extracted with chloroform, and the extract was dried with calcium chloride. The oil remaining after removal of chloroform was vacuum-distilled and yielded:

Frac. I, b.p. 50-100° (5 mm): 2.4 g
Frac. II, b.p. 108-110° (5 mm): 6.5 g; (yield 41.8%)
Residue 0.4 g

	Found %:	Cl 36.45; As 38.44
$C_8H_7Cl_2As$.	Calculated %:	Cl 36.56; As 38.65

Dichlorocyclohexylarsine, dichloromethylarsine, and dichloroethylarsine, which are listed in Table 3, were prepared in a similar way.

13. Decomposition of Bis(2-chlorovinyl)phenylarsine [9] with Alkali. A 30% aqueous solution of caustic soda (30 ml) was added dropwise to 8.7 g of bis(2-chlorovinyl)phenylarsine (b.p. 170-178°/5 mm). The reaction mixture was heated until acetylene ceased to be evolved (1.3 liters, i.e. 91.5% of the calculated amount, was evolved). Of 50 ml of the gas obtained, 42.5 ml was absorbed by Ilosvay's reagent, corresponding to an acetylene content of 85%.

14. Dichlorophenylarsine. When acetylene ceased to be evolved, 100 ml of concentrated hydrochloric acid was added to the reaction mixture, which was then refluxed for six hours. The dark-brown oil that separated was extracted with ether. After removal of ether vacuum distillation of the residue yielded 5.6 g (79.4%) of a colorless liquid, b.p. 100-102° (2 mm); d_4^{13} 1.6410; n_D^{13} 1.6292.

Oxidation of 1 g of dichlorophenylarsine with hydrogen peroxide yielded 0.65 g (71.7%) of pure phenylarsonic acid, m.p. 157.5° (from water). There was no depression in a mixture test with known phenylarsonic acid.

15. (2-Chlorovinyl)dimethylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 61 g of methyl iodide, 100 ml of dry ether, and 52 g of dichloro(2-chlorovinyl)arsine in 250 ml of ether. It is a clear colorless liquid having the characteristic odor of tertiary arsines; b.p. 42° (13 mm); d_4^{20} 1.3923; The yield was 51%.

	Found %:	Cl 21.10; As 44.61
C_4H_8ClAs.	Calculated %:	Cl 21.31; As 45.03

16. Decomposition of (2-Chlorovinyl)dimethylarsine with Alkali. (2-Chlorovinyl)dimethylarsine (20.6 g) was added dropwise to 11.2 g of finely ground caustic potash in 100 ml of ethanol, and the mixture was heated under reflux in a water bath. The gas liberated was collected in a graduated gas holder over saturated brine (2.8 liters of gas, i.e. 99.2%, was evolved). The liquid was filtered from the precipitated potassium chloride, which was then washed with alcohol. Alcohol was distilled off under reduced pressure, and the residual oily liquid of unpleasant odor came over at 118-120° in a stream of carbon dioxide. The yield was 12 g (59.2%);

d_4^{15} 1.4603.

Found %: As 65.82
$C_4H_{12}As_2O$. Calculated %: As 66.35

Of 50 ml of the gas collected in the gas holder, 44.2 ml was absorbed by Ilosvay's reagent, which corresponds to an acetylene content of 88.4%. Chlorodiethylarsine, chlorodiisopropylarsine, dibutylchloroarsine, and chlorodiisopentylarsine were prepared similarly.

17. (2-Chlorovinyl)diphenylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 80 g of bromobenzene, 150 ml of dry ether, and 51 g of dichloro(2-chlorovinyl)arsine in 200 ml of ether. It is a clear colorless liquid having the characteristic odor of tertiaryarsines b.p. 176-178° (3 mm); d_4^{20} 1.3394; n_D^{20} 1.6280; The yield was 57%.

18. Chlorodiphenylarsine. 20.5 g of (2-chlorovinyl)diphenylarsine was decomposed with hot alcoholic alkali; 84.2% of the calculated amount of acetylene was evolved. Alcohol was distilled from the reaction mixture, excess of hydrochloric acid added cautiously to the dry residue, and the mixture was refluxed for one hour in a stream of hydrogen chloride. The oil that separated was extracted with chloroform, and the extract dried with sodium sulfate. Chloroform was distilled off; vacuum-distillation of the residue gave the following fractions.

Found %: Cl 12.03; As 25.55
$C_{14}H_{12}ClAs$. Calculated %: Cl 12.21; As 25.81

The yield of the main fraction (II) was 62.8%. Fraction II was a clear colorless liquid (d_{40}^{40} 1.3522; n_D^{40} 1.6428) that rapidly solidified. After recrystallization from alcohol it had m.p. 37.8-38.3°, undepressed by admixture of known chlorodiphenylarsine.

Oxidation of 1 g of the chlorodiphenylarsine with hydrogen peroxide yielded 0.8 g (83%) of diphenylarsinic acid, m.p. 173-174°, undepressed by admixture of known diphenylarsinic acid. Chlorodi-p-tolylarsine was prepared similarly.

SUMMARY

1. A method was developed for the preparation of primary and secondary alkyl-and aryl-haloarsines; an alkyl- or aryl-(2-chlorovinyl)arsine is split by means of alkali, and the resulting organoarsenic oxide is then treated with hydrochloric acid. The method is general, and it makes it possible to prepare various haloarsines, including some that cannot be prepared by Meyer's reaction. In particular, dichloroisopropyl-, butyldichloro-, dichloroisopentyl-, and dichlorostyryl-arsines can be prepared in satisfactory yields.

2. It is probable that, in the decomposition of alkyl(2-chlorovinyl)arsines with alkalis, alkylethynylarsines are formed, and these then react with water with formation of acetylene and organoarsenic oxides.

Received May 20, 1954

LITERATURE CITED

[1] G. Meyer, Ber. 16, 1440 (1883).

[2] H. Burt, Ann. 423, 174 (1920).

[3] W. M. Dehn, Am. Chem. J. 35, 4? (1906).

[4] E. E. Turner, F. W. Bury, J. Chem. Soc. 1926, 1207, 1443.

[5] W. W. Beck, C. S. Hamilton, J. Am. Chem. Soc. 60, 620 (1938).

[6] C. K. Banks, J. F. Morgan, J. Am. Chem. Soc. 69, 927 (1947).

[7] C. H. Hewett, J. Chem. Soc., 1948, 1203.

[8] W. L. Lewis, H. W. Stiegler, J. Am. Chem. Soc. 47, 2546 (1925).

[9] Nirenja Nath Das Gupta, C. 1936, II, 3089.

[10] O. A. Zeide and I. S. Gorsky, J. Russ. Chem. Soc. 61, 1566 (1929).

[11] V. V. Nekrasov and A. S. Nekrasov, J. Russ. Chem. Soc. 61, 71(1929).

[12] R. Kh. Freidlina, E. I. Brainina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, No 6, 647.

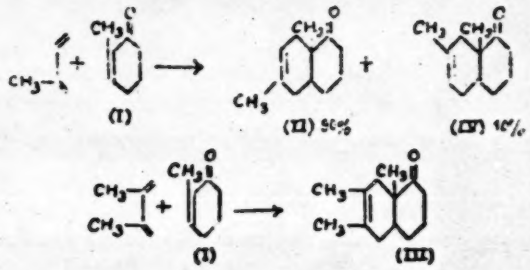
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION 29. CONDENSATION OF ISOPRENE WITH 2-METHYL-2-CYCLOHEXEN-1-ONE. SYNTHESIS OF cis-1,2,4a,5,8,8a-HEXAHYDRO-4a,7-DIMETHYL-4-VINYLNAPHTHALENE

I. N. Nazarov and G. P. Kugatova

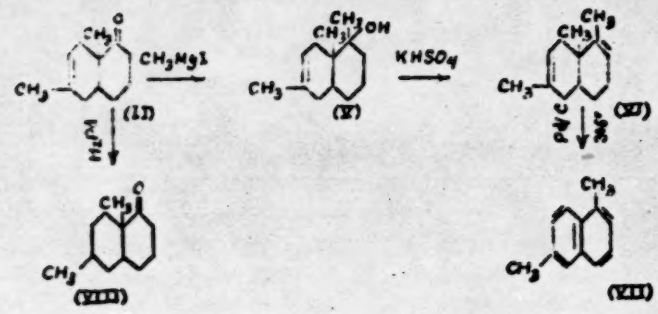
Various bicyclic dienes having angular methyl groups have been applied successfully in our laboratory in condensations with α,β-unsaturated cyclic ketones resulting in the synthesis of a variety of polycyclic compounds having cyclopentaphenanthrene and chrysene skeletons [1]. At the same time interesting observations were made on the spatial structure of the stereoisomeric tetracyclic ketones obtained in this way. However, for the detailed study of the stereochemistry of such compounds, more convenient model examples are provided by adducts formed by bicyclic dienes with such simple dienophiles as mesaconic ester and citraconic anhydride, such as were investigated in relation to the diene 1-vinylcyclohexene [2]. In this connection it was necessary to develop a method for the preparation of the most readily accessible bicyclic diene, and the present investigation was devoted to this problem.

We selected cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) as the original bicyclic ketone containing an angular methyl group; it can be readily obtained by condensing isoprene with 2-methyl-2-cyclohexen-1-one (I) [3]. As a result of a series of experiments under various conditions (temperature, duration, ratio of components), it was shown that the condensation of isoprene with the methylcyclohexenone (I) goes best when the latter is in great excess and when heating is carried out in a nitrogen atmosphere for 45-50 minutes at 260-270°. Under these conditions, the yield of the adduct (II) (b.p. 92-93.5° at 2.5 mm; n_D^{20} 1.5015) was about 64%, based on the methylcyclohexenone that reacted. Under the same conditions cis-3,4,4a,5,8,8a-hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III) was obtained in 60% yield by the condensation of 2,3-dimethyl-1,3-butadiene with 2-methyl-2-cyclohexen-1-one (I):



It has been shown on the basis of numerous examples that various disubstituted dienes, such as isoprene [4], 2-phenyl-1,3-butadiene [5], and 2-methoxy-1,3-butadiene [6], when reacting with unsymmetrical dienophiles yield mixtures of adducts of para and meta structure in which the former predominates greatly. In most of these reactions the yield of meta isomer does not exceed 10-15%, so that its separation from the main product (the para form) is often very difficult.

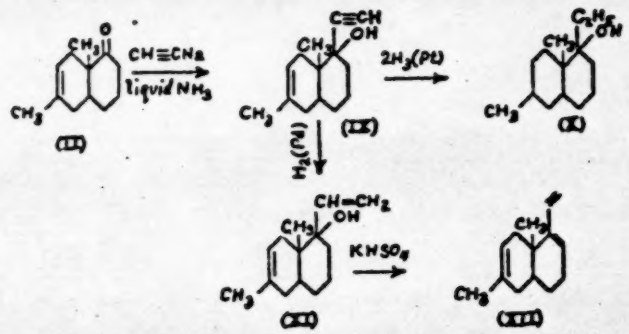
In order to prove the structure of the ketone (II), this was converted by reaction with methylmagnesium iodide into 1,2,3,4,4a,5,8,8a-octahydro-1,6,8a-trimethyl-1-naphthol (V), which was readily dehydrated with potassium hydrogen sulfate into the corresponding 3,4,4a,5,8,8a-hexahydro-1,6,8a-trimethylnaphthalene (VI) (or, with Chem. Abs. numbering, 1,2,4a,5,8,8a-hexahydro-4,4a,7-trimethylnaphthalene). Dehydrogenation of this substance in presence of palladized charcoal (5% Pd) at 350-360° for 36 hours gave a good yield of 1,6-dimethylnaphthalene (VII), identified as the picrate, m.p. 113-114°. These results show that our adduct consisted mainly of cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II). Hydrogenation of the ketone (II) in presence of a palladium catalyst yielded cis-octahydro-6,8a-dimethyl-1(2H)-naphthalenone (VIII):



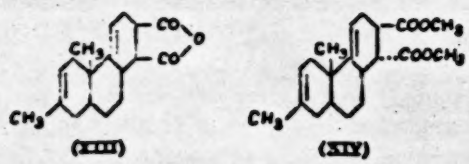
A more detailed investigation carried out in our laboratory has shown that the adduct formed by isoprene with 2-methyl-2-cyclohexen-1-one (I) contains also about 10% of the isomeric cis-hexahydro-7,8a-dimethyl-1(2H)-naphthalenone (IV).

This fact, however, is of no real importance in the subsequent transformations, since it is found that it is then easy to isolate individual products corresponding to the main product (II).

For the preparation of the bicyclic diene from the ketone (II) we used a reaction that has been studied in detail in our laboratory, namely the condensation of cyclic dienes with acetylene in liquid ammonia, followed by partial hydrogenation and dehydration of the ethylenic alcohol [6]. When cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) was condensed with sodium acetylide in liquid ammonia, 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (IX) was obtained in a yield of about 90%



Exhaustive hydrogenation of the acetylenic alcohol (IX) in presence of a platinum catalyst yielded 1-ethyldecahydro-6,8a-dimethyl-1-naphthol (X), and selective hydrogenation in presence of a palladium catalyst gave a good yield of 1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (XI). Dehydration of the ethylenic alcohol (XI) with potassium hydrogen sulfate gave pure cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1-vinylnaphthalene (cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene) (XII) in a yield of about 70%.



The triene (XII) so obtained readily condenses with maleic anhydride and with dimethyl fumarate with formation of the corresponding adducts (XIII) and (XIV) in the form of liquid mixtures of stereoisomers. We intend to devote a special communication to the investigation of these adducts.

EXPERIMENTAL

cis-3,4,4a,5,8,8a-Hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II). A mixture of 180 g of 2-methyl-

2-cyclohexen-1-one (I) (b.p. 55-55.5°/7 mm, n_D^{20} 1.4850 [3]) and 45 g of freshly distilled isoprene was heated at 270-280° for 45-50 minutes in a nitrogen atmosphere in a metal ampoule. Excess of methylcyclohexenone (145 g) was distilled off under reduced pressure. The condensation product from four similar experiments was combined and vacuum-distilled through a Vigreux column. The following fractions were obtained:

Frac. I, b.p. 54-74° (1 mm); n_D^{20} 1.4870; 12 g

Frac. II, b.p. 74-82° (1 mm); n_D^{20} 1.4890; 7.5 g

Frac. III, b.p. 82-84° (1 mm); n_D^{20} 1.5015; 52 g

Redistillation of Fraction III yielded 50 g of cis-3,4,4a,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II), b.p. 92-93.5° (2.5 mm); n_D^{20} 1.5015; d_4^{20} 0.9840; Calculated MR 52.76; Found MR 53.10.

	Found %:	C 80.79; 81.01;	H 10.20; 10.20
$C_{12}H_{18}O$.	Calculated %:	C 80.89;	H 10.11

The semicarbazone obtained from (II) in the usual way had a constant melting point of 219-220° (dec.) after recrystallization from methanol.

	Found %:	N 17.85
$C_{13}H_{21}ON_3$.	Calculated %:	N 17.86

The hexahydro-1(2H)-naphthalenone (II), which was found later to contain about 10% of the meta isomer (IV), was used in all of the reactions described below.

cis-3,4,4a,5,8,8a-Hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III). A mixture of 12 g of 2,3-dimethyl-1,3-butadiene [7] and 30 g of 2-methyl-2-cyclohexen-1-one (I) was heated for 35-40 minutes at 250-255° in a nitrogen atmosphere in a metal ampoule. The excess of methylcyclohexenone was distilled off. Residues from three similar experiments were distilled under reduced pressure and yielded:

Frac. I, b.p. 80-105° (2.5 mm); n_D^{20} 1.5001; 4.5 g

Frac. II, b.p. 105-107° (2.5 mm); n_D^{20} 1.5090; 13.4 g

Redistillation of Fraction II yielded 12.2 g of pure cis-3,4,4a,5,8,8a-hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III), b.p. 106-107.5° (2.5 mm) and n_D^{20} 1.5090.

	Found %:	C 81.34; 81.48;	H 10.52; 10.44
$C_{13}H_{20}O$.	Calculated %:	C 81.20;	H 10.40

The semicarbazone, prepared in the usual way, melted with decomposition at 240-241° after crystallization from butyl alcohol.

	Found %:	N 17.3; 17.15
$C_{14}H_{23}ON_3$.	Calculated %:	N 17.0

Hydrogenation of cis-3,4,4a,5,8,8a-Hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II). The ketone (II) (4 g), dissolved in 200 ml of absolute ether, was hydrogenated in presence of 0.3 g of a palladium catalyst (5% Pd supported on calcium carbonate). In the course of six hours, 571 ml of hydrogen (21°, 738 mm) was absorbed, corresponding to the hydrogenation of one double bond. The catalyst was filtered off, the solvent was distilled off, and the residue was vacuum-distilled. The product was 3.4 g of a substance having b.p. 83-85° (2.5 mm) and n_D^{20} 1.4860. Redistillation yielded 3 g of cis-octahydro-6,8a-dimethyl-1(2H)-naphthalenone (VIII), b.p. 82-83° (1.5 mm); n_D^{20} 1.4855; d_4^{20} 0.9660; Found MR 53.42; Calculated MR 53.23.

	Found %:	C 80.10; 80.28;	H 11.38; 11.06
$C_{12}H_{20}O$.	Calculated %:	C 80.0	H 11.11

The semicarbazone, prepared in the usual way, melted at 207-208° (from 50% methanol).

	Found %:	N 17.43; 17.90
$C_{13}H_{23}ON_3$.	Calculated %:	N 17.71

1,2,3,4,4a,5,8,8a-Octahydro-1,6,8a-trimethyl-1-naphthol (V). A solution of methylmagnesium iodide was prepared from 4.8 g of methyl iodide and 0.7 g of magnesium in 25 ml of absolute ether in a three-necked flask fitted with stirrer, thermometer, dropping funnel, and reflux condenser. The solution was stirred at a temperature not exceeding +10° while slow addition was made of a solution of 4 g of cis-3,4,4a,5,8,8a-hexahydro-

8a-dimethyl-1(2H)-naphthalenone (II) in 10 ml of absolute ether. The mixture was then heated in a water bath at 40° for four hours. With cooling and stirring the reaction product was treated with 10 ml of 1 : 1 hydrochloric acid. The ether layer was separated, washed with a solution of sodium thiosulfate, and dried with magnesium sulfate. Ether was distilled off, and two successive vacuum fractionations of the residue yielded 3 g of pure 1,2,3,4,4a,5,8,8a-octahydro-1,6,8a-trimethyl-1-naphthol (V), b.p. 88-89° (1 mm); n_D^{20} 1.5051; d_4^{20} 0.9783; Found MR 59.23; Calculated MR 58.90.

	Found %:	C 80.28; 80.36;	H 11.19; 11.12
$C_{13}H_{22}O$.	Calculated %:	C 80.41;	H 11.30

Dehydration of 1,2,3,4,4a,8,8a-Octahydro-1,6,8a-trimethyl-1-naphthol (V). A mixture of 3 g of the octahydrotrimethylnaphthol (V) and 1.5 g of anhydrous potassium hydrogen sulfate was heated at 150-160° in a Claisen flask for one hour. A little water was added to dissolve the potassium hydrogen sulfate, and the dehydration product was extracted with ether. The extract was dried with magnesium sulfate, and ether was distilled off. Vacuum distillation of the residue yielded 1.5 g of the dehydration product, b.p. 86-90° (10 mm), which was redistilled over sodium and gave 1.2 g of 1,2,4a,5,8,8a-hexahydro-4,4a,7-trimethylnaphthalene (VI), b.p. 86-88° (10 mm); n_D^{20} 1.4580; d_4^{20} 0.9390. The hydrocarbon was dehydrogenated without further purification.

Dehydrogenation of 1,2,4a,5,8,8a-Hexahydro-4,4a,7-trimethylnaphthalene (VI). A mixture of 1.2 g of the hexahydrotrimethylnaphthalene (VI), 1 g of palladized charcoal (5% Pd), and 5 ml of cryoscopic benzene was heated for 36 hours at 350-360° in a metal ampoule. The catalyst was filtered off and washed with ether. Vacuum distillation of the residue remaining after removal of solvents yielded 0.6 g of 1,6-dimethylnaphthalene (VII), b.p. 105-107° (10 mm); n_D^{20} 1.5690. Its picrate, prepared in the usual way and crystallized from ethanol, had m.p. 113-114°, undepressed by admixture of known 1,6-dimethylnaphthalene picrate [8].

1-Ethynyl-1,2,3,4,4a,5,8,8a-Octahydro-6,8a-dimethyl-1-naphthol (IX). Liquid ammonia (600 ml) was introduced into a two-liter three-necked flask fitted with stirrer, thermometer, tube for passage of gas, and dropping funnel. Sodium (19 g) was added slowly at a temperature of −70°. The mixture was stirred for 30 minutes, and when the sodium had dissolved, dry acetylene was passed for two hours at 25-30 liters per hour. The resulting solution of sodium acetylide was stirred while, with continued passage of acetylene, a solution of 50 g of cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) in 100 ml of absolute ether was added slowly (over a period of 90 minutes). The mixture was then stirred for one hour, after which it was set aside overnight. The temperature of the reaction mixture was maintained at −70° throughout the reaction and during the night. On the next day much of the liquid ammonia was distilled off, and at −30° 250 ml of ether, 45 g of ammonium chloride (in small portions), and 270 ml of water were added. The ether layer was separated and the aqueous layer was extracted three times with 200-ml portions of ether. The united ether extract was washed twice with a 1% solution of hydrochloric acid and then dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum-distilled. Two successive distillations yielded 49.5 g (87%) of the acetylenic alcohol (IX), b.p. 94-95° (1.5 mm); n_D^{20} 1.5210.

	Found %:	C 81.99; 81.91;	H 9.89; 10.03
$C_{14}H_{20}O$.	Calculated %:	C 82.25;	H 9.86

1-Ethyldecahydro-6,8a-dimethyl-1-naphthol (X). The acetylenic alcohol (IX) (2 g) was dissolved in 10 ml of ethanol and hydrogenated in presence of platinum oxide. In the course of three hours 660 ml of hydrogen (21°, 738 mm) was absorbed, which corresponds to the hydrogenation of three double bonds. Solvent was distilled off, and the hydrogenation product was distilled twice under reduced pressure. The product was 1.6 g of 1-ethyldecahydro-6,8a-dimethyl-1-naphthol (X), b.p. 103-104° (2 mm); n_D^{20} 1.5030.

	Found %:	C 79.78; 79.68;	H 11.84; 11.98
$C_{14}H_{26}O$.	Calculated %:	C 79.98;	H 12.20

1,2,3,4,4a,5,8,8a-Octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (XI). 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-naphthol (IX) (20 g) was dissolved in 250 ml of ethanol and hydrogenated over a palladium catalyst (5% Pd supported on calcium carbonate). In the course of two hours, 2.3 liters of hydrogen (21°, 736 mm) was absorbed, corresponding to the hydrogenation of one double bond, and the process was then discontinued. The catalyst was filtered off, solvent was distilled off, and the hydrogenation product was vacuum-distilled.

The following fractions were obtained:

Frac. I, b.p. 104-107° (3 mm); n_D^{20} 1.5160; 3.6 g
Frac. II, b.p. 107-108° (3 mm); n_D^{20} 1.5185; 15.2 g

Refractionation of Fraction II yielded 14.2 g (72%) of the pure ethylenic alcohol (XI), b.p. 107-107.5° (3 mm); n_D^{20} 1.5180.

	Found %:	C 81.25; 81.13;	H 10.86; 10.62
$C_{14}H_{22}O_2$.	Calculated %:	C 81.42;	H 10.62

1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII). A mixture of 15 g of the ethylenic alcohol (XI) (b.p. 107-107.5°/3 mm, n_D^{20} 1.5180), 1.2 g of anhydrous potassium hydrogen sulfate, and 0.1 g of pyrogallol was heated at 130-135° and a residual pressure of 70 mm in a stream of nitrogen in a Claisen flask for 25 minutes. Water was distilled off, and the dehydration product was vacuum-distilled. The product was 12.4 g of the crude triene (XII), b.p. 111-114° (7 mm) and n_D^{20} 1.5155, and this was subjected to further dehydration by distillation over 0.5 g of anhydrous potassium hydrogen sulfate. The product, finally purified by distillation over sodium, was 9.1 g (a cut 70°) of pure 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII), b.p. 109-110° (8 mm), n_D^{20} 1.5160.

	Found %:	C 88.85; 88.99;	H 10.90; 10.86
$C_{14}H_{22}$.	Calculated %:	C 89.30;	H 10.70

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) with Maleic Anhydride. A mixture of 4 g of the triene (XII) (b.p. 109-110°/8 mm and n_D^{20} 1.5160) and 1.6 g of freshly distilled maleic anhydride was heated in presence of a little pyrogallol at 100° for three hours in a sealed glass tube. Unchanged triene and maleic anhydride were removed under reduced pressure, and the thick yellow oil that remained was distilled in a high vacuum. The following fractions were obtained:

Frac. I, b.p. 125-185° (0.025 mm): 1.2 g
Frac. II, b.p. 195-200° (0.025 mm): 3.6 g

Redistillation of Fraction II yielded 3 g of a thick light-yellow liquid, b.p. 197-200° (0.025 mm), corresponding in composition to the adduct (XIII).

	Found %:	C 75.95; 76.0	H 7.92; 8.09
$C_{18}H_{24}O_3$.	Calculated %:	C 75.76;	H 7.80

The adduct (XIII) did not crystallize when treated with solvents and did not give a crystalline substance when hydrolyzed.

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) with Dimethyl Fumarate. A solution containing 7 g of the triene (XII) and 5.3 g of dimethyl fumarate in 25 ml of benzene was heated in a metal ampoule at 200-210° for four hours. Solvent was distilled off, and crystals of dimethyl fumarate that separated were filtered off. The filtrate – a thick oil – was vacuum-distilled and yielded 4.1 g of the condensation product, b.p. 148-150° (0.02 mm), corresponding in composition to the adduct (XIV).

	Found %:	C 72.31; 72.38	H 8.45; 8.55
$C_{22}H_{32}O_4$.	Calculated %:	C 72.27;	H 8.47

After hydrolysis of the product with 20% caustic potash solution no individual crystalline substances could be isolated.

SUMMARY

1. The condensation of isoprene with 2-methyl-2-cyclohexen-1-one (I) was studied, and it was shown that the main product of this reaction is the para isomer, cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II), the structure of which was proved by its conversion into 1,6-dimethylnaphthalene (VII).

2. Condensation of the hexahydro-1(2H)-naphthalenone (II) with sodium acetylide in liquid ammonia gave a 90% yield of the acetylenic alcohol (IX), which was converted by selective hydrogenation into the ethylenic alcohol (XI). Dehydration of (XI) gave 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) in an overall yield, taken over all stages, of more than 50%.

3. The cis triene (XII) was condensed with maleic anhydride and with dimethyl fumarate, and mixtures of stereoisomeric adducts (XIII) and (XIV) were obtained in high yield.

LITERATURE CITED

[1] I. N. Nazarov, G. P. Verkholetova, L. V. Torgov, and I. I. Zaretskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 5, 920, 929; I. N. Nazarov, L. I. Shmonina, and L. V. Torgov, Bull. Acad. Sci. USSR, Div. Chem Sci 1953, No. 6, 1074.••

[2] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 78, 89.•••

[3] I. N. Nazarov, L. D. Bergelson, I. V. Torgov, and S. N. Ananchenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 5, 889. ••••

[4] K. Alder, W. Vogt, Ann. 564, 109 (1949); L. Miller, D. Mann, J. Am. Chem. Soc. 72, 1484 (1950); J. Meek, R. Merrow, S. Cristol, J. Am. Chem. Soc. 74, 2667 (1952); I. N. Nazarov et al., J. Gen. Chem. 25, 88 (1955). •••••

[5] J. Meek, R. Merrow, D. Ramay, J. Am. Chem. Soc. 73, 5563 (1952).

[6] I. N. Nazarov, I. V. Torgov, I. I. Zaretskaya, G. P. Verkholetova, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 1, 78.••••••

[7] Organic Syntheses, Vol. 3, Foreign Lit. Press, Moscow, 1952, p. 187.

[8] I. Heilbron and H. M. Bunbury, Dictionary of Organic Compounds, Vol. 3, Foreign Lit. Press, Moscow, 1949, p. 492.

Received July 22, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

---

• Consultant 's Bureau Translation, p.817, 827.

•• Consultant's Bureau Translation, p.955.

••• Consultant's Bureau Translation, p.67, 77.

•••• Consultant's Bureau Translation, p.787.

••••• Consultant's Bureau Translation, p.75.

•••••• Consultant's Bureau Translation, p.69.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

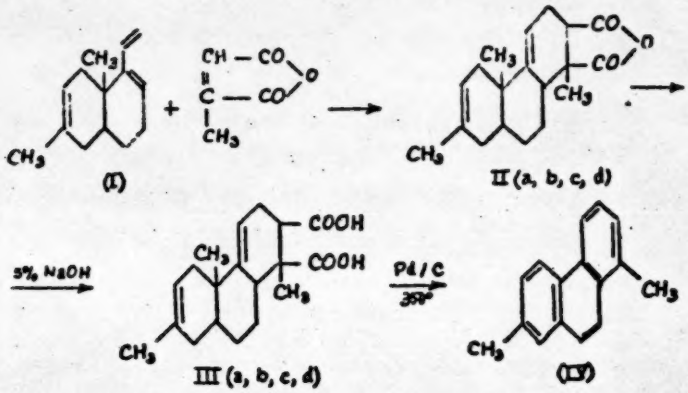
COMMUNICATION 8. CONDENSATION OF cis-1,2,4a,5,8,8a-HEXAHYDRO-4a,7-DIMETHYL-4-VINYLNAPHTHALENE WITH CITRACONIC ANHYDRIDE

I. N. Nazarov, V. F. Kucherov, and G. P. Kugatova

The diene condensations of 1-vinylcyclohexene with citraconic anhydride [1] and with dimethyl mesaconate [2] have made it possible to study some of the stereochemical transformations of bicyclic ortho-dicarboxylic acids and to make some interesting inferences relating to the dependence of their reactivities on their spatial structures. With the object of making a further study of the sterochemistry of cyclic compounds we have investigated the condensation of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) [3] with citraconic anhydride. When a mixture of these components (70-80% excess of diene) was heated at 100° for ten hours, a 30% yield was obtained of a mixture of four stereoisomeric crystalline anhydrides [(II): a, b, c, and d] which were separated by fractional crystallization.

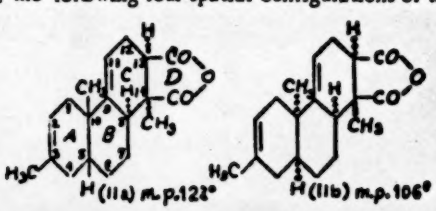
These isomeric anhydrides were isolated in the proportions 16 : 16 : 2 : 1, and when they were hydrolyzed with 5% caustic soda solution, the corresponding individual crystalline stereoisomeric cis acids [(III): a, b, c, and d] were obtained.

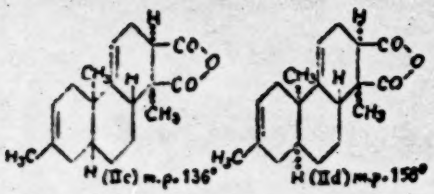
The proportions in which the crystalline isomers are formed in the diene synthesis were found to vary somewhat with temperature, and at 20° (10 days) very little of the isomer (IIc) was obtained. When reaction was at room temperature for one day and then at 100° for 10 hours, the amounts of the isomers (IIc) and (IId) were increased appreciably, though the isomers (IIa) and (IIb) were always the main reaction products.



The identity of the ring structure present in the isomeric dicarboxylic acids [(III): a, b, c, and d] was proved by dehydrogenation over palladized charcoal (5% Pd) at 340-350°. The only product from all four isomers was 1,7-dimethylphenanthrene (IV), which was characterized as its picrate and styphnate. These results show that all four of the isomeric anhydrides (II) isolated in the synthesis described have the same phenanthrene skeleton and differ only insteric structure. These anhydrides were formed as a result of ortho addition; attempts to detect adducts formed by para addition in the products of the diene synthesis were not successful.

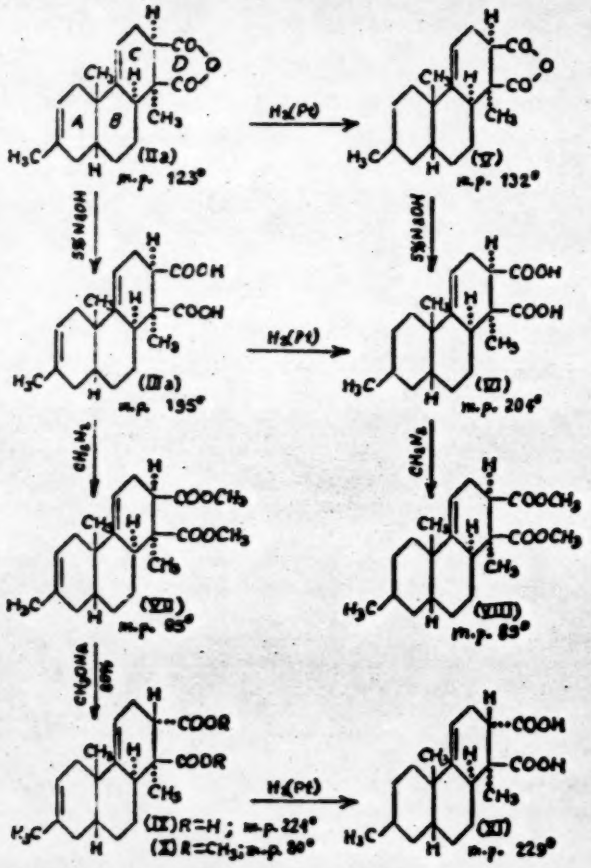
In accordance with the method of preparation (two-fold diene synthesis), for the anhydrides (II), which have five centers of asymmetry, the following four spatial configurations of the cis-cis series are possible:





In view of the relative mildness of the condensation conditions (up to 100°), it may be considered that each of the four isomeric anhydrides isolated has a double bond in the normal position (C-9)–(C-11)• and that the two isomers formed in predominating amounts, (IIa) and (IIb), have spatial structures corresponding, according to molecular models, to endo addition. These suppositionswere fully confirmed by a study of the chemical transformations of the isomers, so that their spatial configurations have been proved.

When the cis anhydride (IIa) was hydrogenated in benzene or acetic anhydride in presence of a platinum catalyst, only one molecular porportion of hydrogen was absorbed, with formation of the individual anhydride (V), which gave the corresponding acid (VI) when hydrolyzed. The same acid was formed when the cis acid (IIIa), obtained by hydrolysis of the anhydride (IIa), was hydrogenated. Treatment of the cis acid (IIIa) with an ether solution of diazomethane gave the corresponding diester (VII), m.p. 95°, and this again absorbed only one molecular proportion of hydrogen when hydrogenated in presence of a platinum catalyst, the individual diester (VIII), m.p. 85°, being formed. In accordance with its cis structure, the diester (VII) gave a good yield of the trans acid (IX) when isomerized with sodium methoxide, and this acid gave the trans diester (X) with diazomethane and the individual trans acid (XI), formed by absorption of one molecular proportion of hydrogen, when hydrogenated over a platinum catalyst.

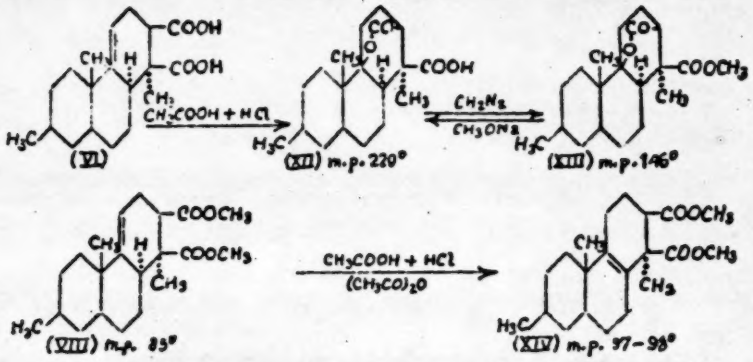


• Steroid numbering.

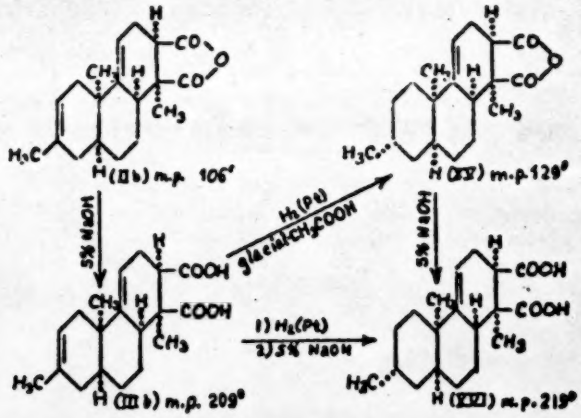
A characteristic feature of the compounds (IIa), (IIIa), (VII), and (IX) is the selectivity of hydrogenation, which only affects one double bond with formation of an individual product from each of these compounds. As shown previously [4], in such polycyclic compounds the double bond at (C-9) – (C-11) is considerably more difficult to hydrogenate than a double bond in the ring A. On this basis it may be supposed that in our experiments only the double bond in the ring A undergoes hydrogenation, and, owing to the cis configuration of the rings A and B, addition of hydrogen occurs from the unscreened side (opposite to the substituents at C-5 and C-10) and results in the cis configuration of the methyl group at C-3. As will be shown below, similar sterically selective hydrogenation of the double bond of the ring A is observed in all other similar compounds described in this communication. The position of the remaining double bond in the hydrogenation products was proved by subsequent lactonization and isomerization.

When the cis acid (VI) was heated with a mixture of acetic acid and dry hydrogen chloride, the cis lactone acid (XII), m.p. 220°, was formed. Titration of this showed that it contained one free carboxyl group, and treatment with diazomethane yielded the cis lactone ester (XIII). According to results obtained previously for bicyclic dicarboxylic acid [5], such lactonization is possible only when there is a double bond in the ring C. The lactone acid (XII) is a δ-lactone, for its ester (XIII) does not isomerize when boiled for a long time with sodium methoxide, but is hydrolyzed with formation of the original cis lactone acid (XII) in good yield.

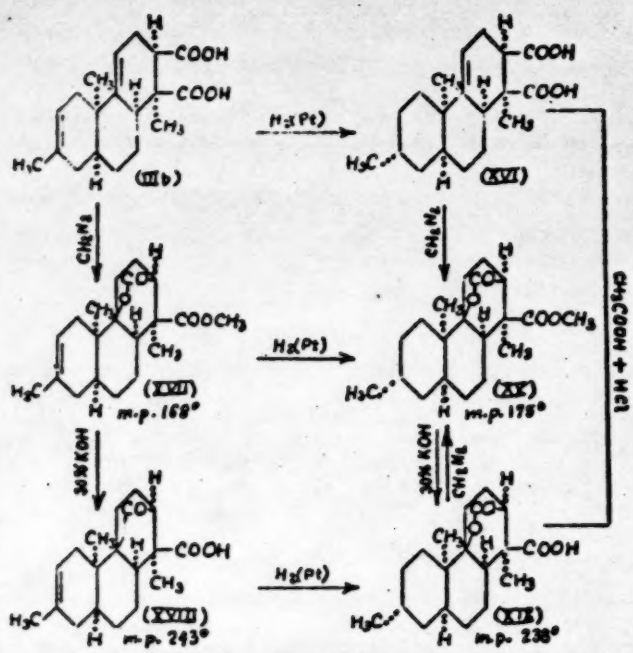
The presence of a double bond at (C-9) – (C-11) in the acid (VI) was proved by the fact that the corresponding cis diester (VIII), treated under the conditions for double-bond migration (action of a mixture of glacial acetic acid, acetic anhydride, and hydrogen chloride), gave the new cis diester (XIV), m.p. 97-98°, having an interring double bond and identical with the substance obtained from the isomeric cis diester (XXV) (see below):



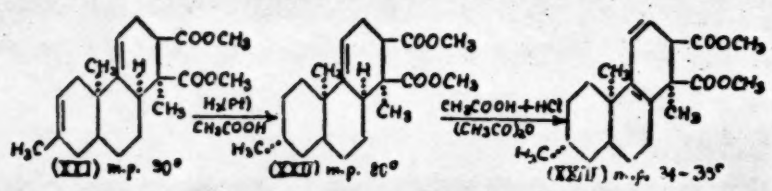
We have also studied some of the chemical transformations of the isomeric cis anhydride (IIb). Hydrolysis of this anhydride with 5% caustic soda gave the corresponding cis acid (IIIb) and, when this was hydrogenated in acetic acid in presence of a platinum catalyst, one molecular proportion of hydrogen was absorbed with simultaneous elimination of water and formation of the anhydride (XV). Hydrolysis of this gave the pure cis acid (XVI), which was different from the isomeric cis acid (VI):



Unlike the cis acids (IIIa) and (VI), the isomeric acids (IIIb) and (XVI) have a very strong tendency to undergo lactonization. Thus, when the cis acid (IIIb) was treated with a pure ethereal solution of diazomethane, the main product was not the diester, as it was for the isomeric cis acid (IIIa), but the crystalline cis lactone ester (XVIII), which undergoes hydrogenation with absorption of one molecular proportion of hydrogen and formation of the saturated lactone acid (XVI). Again, the main product of the reaction of diazomethane with the acid (XVI) is not the corresponding diester, but the saturated cis lactone ester (XX), which is obtained also when the cis lactone ester (XVII) is hydrogenated. Hydrolysis of the cis lactone ester (XX) gave the saturated cis lactone acid (XIX) in high yield.



In the reaction of diazomethane with the cis acid (IIIb), only a small amount of the corresponding cis diester (XXI) was isolated. Hydrogenation of this diester in presence of a platinum catalyst yielded the cis diester (XXII) by absorption of one molecular proportion of hydrogen. Under the conditions for double-bond migration (action of a mixture of acetic anhydride, glacial acetic acid, and hydrogen chloride) the cis diester (XXII) gave the new diester (XXIII), m.p. 34-35°, having an inter-ring double bond and differing from the cis diester (XIV) obtained by the same method from the isomeric diester (VIII).

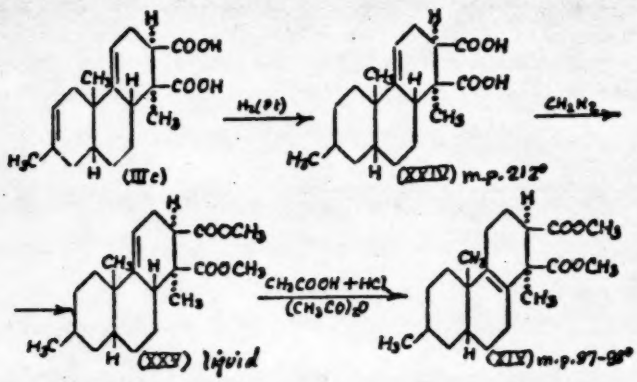


The fact that displacement of the double bond into the inter-ring position in the isomeric diesters (VIII) and (XXII), though causing the elimination of the same center of asymmetry at C-8, yields different products shows that the original isomeric cis anhydrides (IIa) and (IIb) are not epimeric at C-8, but differ in the relative configurations of the rings A – B and C – D, so that they have different arrangements of the angular methyl group at C-10. In accordance with this view, the acid (IIIb) should be relatively prone to lactonization, the 10-methyl and 13-carboxyl being in a trans arrangement, whereas the acid (IIIa), with a cis arrangement of these groups, should undergo lactonization with difficulty owing to the screening effect of th 10-methyl. Subsequent study of

some reactions of the third isomeric cis acid (IIIc) enabled us to prove conclusively the spatial structures of the cis acids (IIIa) and (IIIc), as epimeric at C-8.

When the cis acid (IIIc) was hydrogenated over a platinum catalyst, again only one molecular proportion of hydrogen was absorbed with formation of the individual cis acid (XXIV), which readily gave the corresponding cis diester (XXV), a liquid, with diazomethane.

The formation of this cis diester was not accompanied by lactonization, and under the conditions of double-bond migration the diester readily gave the above-described cis diester (XIV), m.p. 97-98°, formed also by displacement of the double bond in the isomeric cis diester (VIII).



These facts show that the isomeric cis acids (IIIa) and (IIIc) differ only in the disposition of hydrogen at C-8, and the cis arrangement of the 10-methyl, 8-hydrogen, and 13-carboxyl in the acid (IIIc), makes it more stable to lactonization than the isomeric cis acid (IIIb). Owing to the low accessibility of the fourth isomeric cis acid (IIId), it was not investigated further. However, from the conditions of its formation there is no reason to suppose that it differs from the other three isomeric acids in the position of the double bond, and it should be an epimer of the acid (IIIb), differing from this only in the disposition of hydrogen at C-8.

The described diene condensation of the hexahydrovinylnaphthalene (I) with citraconic anhydride has a similar course, structurally and sterically, to the condensations of bicyclic dienes with α,β-unsaturated ketones previously investigated in our laboratory [4].

EXPERIMENTAL

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) with Citraconic Anhydride

1. A mixture of 15.2 g of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (b.p. 109-110.5°/8mm; n_D^{20} 1.5160) [3], 5.3 g of citraconic anhydride (n_D^{20} 1.4710), and 0.2 g of pyrogallol was heated in a nitrogen atmosphere in a sealed glass tube at 100° for ten hours. The liquid reaction product was dissolved in an equal volume of petroleum ether and the solution was set aside at room temperature overnight; 2.7 g of crystals, m.p. 108-121° separated (Fraction A). The mother liquor was diluted with 5 ml of petroleum ether and cooled to − 10°, and after 5-6 hours a further 0.5 g of crystals, m.p. 121-128°, was isolated (Fraction B). From the filtrate excess of the original diene and unchanged citraconic anhydride (3.5 g) were removed by vacuum distillation, and the thick yellow residue was dissolved in an equal volume of petroleum ether with the addition of 1 ml of absolute benzene. The solution was set aside overnight at room temperature, and 3.2 g of crystals melting at 95-107° separated (Fraction C). The total yield of crystalline mixtures of anhydrides was 6.4 g (45% on the citraconic anhydride). We did not succeed in separating any other crystalline anhydrides from the liquid residue (5 g).

Fraction A (2.7 g) was boiled for 1-2 minutes with 50 ml of petroleum ether, and the undissolved portion was filtered off (1.4 g, m.p. 117-121°) and again boiled with 25 ml of petroleum ether. From the cooled filtrates 1.8 g of pure crystalline cis anhydride (IIa) separated in the form of short fine needles, m.p. 122-123°. Recrystallization from petroleum ether did not affect the melting point.

	Found %:	C 76.0 75.80:	H 8.10; 8.30
$C_{19}H_{24}O_3$.	Calculated %:	C 75.96;	H 8.05

Hydrolysis of the cis anhydride (IIa) was effected by boiling 0.22 g with 3 ml of 5% caustic soda solution. Acidification yielded 0.2 g of acid, m.p. 184-186°. Two successive crystallizations from 60% methanol yielded 0.17 g of pure cis acid (IIIa), m.p. 194-195° (dec).

	Found %:	C 71.70; 71.78:	H 8.30; 8.25
$C_{19}H_{28}O_4$.	Calculated %:	C 71.56;	H 8.23

The crystalline substance (0.7 g) that remained, undissolved by petroleum ether, after the separation of the cis anhydride (IIa) was dissolved by prolonged boiling in 25 ml of petroleum ether. When the solution was cooled, 0.36 g of crystals, m.p. 120-125°, separated. They were boiled with 10 ml of petroleum ether for 1-2 minutes, and the undissolved residue was filtered off. When cooled, the mother liquor yielded 0.2 g of the cis anhydride (IIa), m.p. 122-123°. The undissolved residue was crystallized from 6 ml of a 5 : 1 mixture of petroleum ether and benzene and yielded 50 mg of pure cis anhydride (IIc) in the form of small plates having a constant m.p. 135-136°.

	Found %:	C 75.60; 75.82;	H 8.09; 8.09
$C_{19}H_{24}O_3$.	Calculated %:	C 75.96;	H 8.05

Hydrolysis of this anhydride with 5% caustic soda solution and crystallization of the product from aqueous acetone yielded pure cis acid (IIIc), m.p. 202-203° (dec.).

	Found %:	C 71.67; 71.48;	H 8.35; 8.39
$C_{19}H_{28}O_4$.	Calculated %:	C 71.56;	H 8.23

Fraction B (0.5 g of crystals, m.p. 121-128°) was boiled with 5 ml of petroleum ether for 3-5 minutes, and the undissolved portion was filtered off. The cooled filtrate yielded a further 0.1 g of the cis anhydride (IIa), m.p. 122-123°. The substance not dissolved by petroleum ether (0.17 g, m.p. 123-129°) was crystallized twice from a 5 : 1 mixture of petroleum ether and benzene and yielded 10 mg of pure crystalline cis anhydride (IId) in the form of long needles having a constant m.p. of 156-157°.

	Found %:	C 76.16;	H 8.02
$C_{19}H_{24}O_3$.	Calculated %:	C 75.96;	H 8.05

Hydrolysis of this anhydride with 5% caustic soda solution, followed by crystallization of the product from aqueous acetone, yielded pure cis acid (IIId), m.p. 180-181° (dec.).

	Found %:	C 71.26;	H 8.33
$C_{19}H_{28}O_4$.	Calculated %:	C 71.56;	H 8.23

Fraction C (3.2 g of crystals, m.p. 95-107°) was recrystallized from ether and yielded 2.2 g of an apparently pure anhydride (large plates, m.p. 120-130°). Further crystallizations from various solvents did not narrow the melting range. This anhydride was hydrolyzed at the boil with excess of 5% caustic soda solution, and the crystalline acid was recrystallized from 5% acetic acid. The product was 1.6 g of pure cis acid (IIIb), melting constantly at 208-209°.

	Found %:	C 71.81; 71.87;	H 8.45; 8.40
$C_{19}H_{28}O_4$.	Calculated %:	C 71.56;	H 8.23

The cis acid (IIIb) was readily converted into its anhydride by treatment with acetic anhydride at the boil for two hours. Acetic anhydride was distilled off, and the crystalline residue was crystallized twice from petroleum ether. The product was pure cis anhydride (IIb), melting constantly at 105-106.5°.

	Found %:	C 75.80; 76.0;	H 8.23; 8.18
$C_{19}H_{24}O_3$.	Calculated %:	C 75.96;	H 8.05

The liquid residue (5 g) remaining after separation of the crystalline anhydride fractions (A, B, and C) was hydrolyzed and yielded 2.5 g of acid. Crystallization of this from 60% methanol yielded 1.4 g of pure cis acid (IIIa), m.p. 194-195° (dec.).

2. A mixture of 20 g of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I), 7 g of citraconic anhydride, and 0.2 g of pyrogallol was sealed in a tube in a nitrogen atmosphere. The mixture was set aside at room temperature, and after some time, during which it was periodically shaken, it became homogeneous. After 15-18 hours the reaction mixture was heated to 100° and kept at this temperature for ten hours. The solution was diluted with an equal volume of petroleum ether and set aside overnight; 2.1 g of crystals, m.p. 110-119°

separated (Fraction A). The filtrate, after being diluted with 5 ml of petroleum ether and cooled to –20°, yielded a further 0.4 g of crystalline adduct, m.p. 114-124° (Fraction B).

Excess of the triene (I) and unchanged citraconic anhydride were distilled from the filtrate under reduced pressure, and the liquid residue was dissolved in an equal volume of petroleum ether with the addition of 2-3 ml of benzene. The crystals that separated after two hours at room temperature were filtered off, and 4.1 g of adduct melting at 85-103° was obtained (Fraction C). Petroleum ether was partially removed from the mother liquor, and this then yielded a further 3.1 g of crystals, m.p. 84-89° (Fraction D).

Fractional crystallization of Fraction A from petroleum ether, as described above, yielded 1.4 g of cis anhydride (IIa), m.p. 122.5-123.5°, and 0.15 g of cis anhydride (IIc), m.p. 135-136°. Fraction B (0.4 g of crystals) was recrystallized from a 1 : 5 mixture of benzene and petroleum ether, and the resulting mixture of crystals (large plates and needles) was sorted out by hand. Crystallizations from a 1 : 5 mixture of benzene and petroleum ether yielded 0.1 g of the cis anhydride (IIc), m.p. 135-136°, and 0.2 g of the cis anhydride (IId), m.p. 156-157°. Fraction C, m.p. 85-103°, was recrystallized from a 1 : 1 mixture of benzene and heptane, and the resulting nonhomogeneous anhydride (2.6 g, m.p. 113-120°) was hydrolyzed with 5% caustic soda solution. Crystallization from 50% acetic acid yielded 2.2 g of pure cis acid (IIIb), m.p. 208-209° (dec.). Fractional crystallization of Fraction D, m.p. 84-89°, from petroleum ether yielded 1.1 g of the cis anhydride (IIIa), m.p. 122-123°, and 0.15 g of pure cis anhydride (IIIb), m.p. 105-106.5°.

Dehydrogenation of the Isomeric cis Acids (III; a, b, c, and d)

1. A mixture of 0.3 g of the cis acid (IIIa), m.p. 194-195°, 0.15 g of palladized charcoal (5 % Pd), and 7 ml of absolute benzene was heated in a steel ampoule for one hour at 140-150° and then for two hours at 340-350°. The catalyst was filtered off, the solvent was distilled off, and the residue was converted in the usual way into a picrate (m.p. 122-125°), from which 80 mg of a crystalline hydrocarbon was isolated by decomposition with alkali. Crystallization from a little absolute methanol yielded 65 mg of 1,7-dimethylphenanthrene, m.p. 83-84°, which gave a picrate, m.p. 130-131°, and styphnate, m.p. 158-159°.

2. In a similar way, dehydrogenation of 0.3 g of the cis acid (IIIb) yielded, after crystallization from methanol, 75 mg of 1,7-dimethylphenanthrene, m.p. 83-84°, which gave a styphnate melting at 157-158°. The isomeric cis acids (IIIc) and (IIId) were dehydrogenated in the same way. The constants of the hydrocarbons obtained, and of their derivatives, are given in the following table.

TABLE

Hydrocarbon	M.p. (°C)		
	of hydrocarbon	of picrate	of styphnate
1,7-Dimethylphenanthrene [6]	85	131-132	159
Hydrocarbon from (IIIa)	83-84	130-131	158-159
Hydrocarbon from (IIIb)	83-84	–	157-158
Hydrocarbon from (IIIc)	–	130-131	–
Hydrocarbon from (IIId)	80-82	129-130	–
2,6-Dimethylphenanthrene [6]	101	154	–

Hydrogenation of the cis Anhydride (IIa)

The cis anhydride (IIa) (0.5 g; m.p. 122.5-123.5°) was dissolved in 50 ml of cryoscopic benzene and hydrogenated in presence of a platinum catalyst. In the course of one hour 85 ml of hydrogen (24°, 744 mm) was absorbed (one molecular proportion), and hydrogenation then ceased. Catalyst was separated and solvent was distilled off, and crystallization of the crystalline residue from petroleum ether yielded 0.37 g of pure cis anhydride (V), m.p. 131-132°.

$C_{13}H_{26}O_3$. Found %: C 75.51; 75.63; H 8.60; 8.63
Calculated %: C 75.45; H 8.67

a) The cis acid (IIIa) (0.2 g; m.p. 194-195°) was dissolved in 20 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 20 ml (one molecular proportion) of hydrogen had been absorbed. The solvent was distilled off, and the liquid residue was hydrolyzed with 5% caustic soda solution. The product was 0.16 g of the cis acid (VI), which after crystallization from 70% aqueous acetone melted constantly (with decomposition) at 203-204°.

$C_{13}H_{22}O_4$. Found %: C 71.05; 71.29; H 8.84; 8.87
Calculated %: C 71.22; H 8.80

b) A mixture of 0.15 g of the cis anhydride (V) and 12 ml of 5% caustic soda solution was refluxed until a solution was obtained. Acidification of the solution yielded 0.1 g of the cis acid (VI), m.p. 202-203°, undepressed in an admixture of the product of the previous experiment.

cis Diester (VII)

A suspension of 0.3 g of the cis acid (IIIa) in 10 ml of ether was treated with excess of an ether solution of diazomethane. The liquid residue remaining after removal of ether crystallized when treated with petroleum ether, and 0.25 g of the cis diester (VII), melting constantly at 95-95.5°, was obtained.

	Found %:	C 72.91; 72.75; H 8.75; 8.85
$C_{21}H_{36}O_4$.	Calculated %:	C 72.79; H 8.72

cis Diester (VIII)

a) The cis diester (VII) (0.1 g; m.p. 95-95.5°) was dissolved in 7 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 8.5 ml (one molecular proportion) of hydrogen had been absorbed. The solvent was distilled off, and the liquid residue gradually solidified when evaporated under reduced pressure with ligroin. The completely solid material was crystallized from petroleum ether, and 0.07 g of pure cis diester (VIII), m.p. 85.5-86°, was obtained.

	Found %:	C 71.99; 72.27; H 9.35; 9.21
$C_{21}H_{38}O_4$.	Calculated %:	C 72.37; H 9.25

b) When an ether suspension of 0.1 g of the cis acid (VI) was treated with an ether solution of diazomethane, the product, obtained after removal of ether and crystallization of the residue from petroleum ether, was 0.08 g of the diester (VIII), m.p. 85-86°, identical with the product of the previous experiment.

Isomerization of the cis Diester (VII)

The cis diester (VII) (0.4 g) was added to a solution of 1 g of sodium in 25 ml of absolute methanol, and the solution was boiled for 18 hours. The bulk was reduced by one-quarter by removal of methanol, 8 ml of water was added, and the solution was again boiled for five hours, after which it was evaporated down in a porcelain dish on a water bath to a thick slurry. The precipitate of salts was filtered off and suspended in water. Acidification of the suspension to Congo red yielded 0.35 g of acid, m.p. 196-199°, which was crystallized twice from 60% aqueous methanol and yielded 0.2 g of pure trans acid (IX), m.p. 222-224° (dec.).

	Found %:	C 71.70; 71.67; H 8.09; 8.07
$C_{19}H_{32}O_4$.	Calculated %:	C 71.56; H 8.23

The trans acid (IX) was treated with an ether solution of diazomethane and the product was crystallized from petroleum ether. A good yield of the trans diester (X), m.p. 79.5-80°, was obtained.

	Found %:	C 72.64; 72.84; H 8.80; 8.72
$C_{21}H_{36}O_4$.	Calculated %:	C 72.79; H 8.72

Hydrogenation of the trans Acid (IX)

The trans acid (IX) (0.2 g; m.p. 222-224°) was dissolved in 12 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Only one molecular proportion of hydrogen was absorbed (17 ml). Solvent was distilled off, and the crystalline residue was washed on the filter with a 1 : 1 mixture of benzene and petroleum ether. Recrystallization from 80% aqueous acetone yielded 0.16 g of the trans acid (XI), m.p. 228-229.5° (dec.), depressed by admixture of the original acid (200-210°).

	Found %:	C 71.20; 71.38; H 8.89; 8.97
$C_{19}H_{34}O_4$.	Calculated %:	C 71.22; H 8.80

cis Lactone Acid (XII)

A mixture of 0.2 g of the cis acid (VI), m.p. 203-204° and 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The crystals remaining after removal of acetic acid by distillation were washed on the filter with benzene. Crystallization from 70% aqueous methanol yielded 0.15 g of pure cis lactone acid (XII), m.p. 219-220°.

	Found %:	C 71.03; 71.28; H 8.94; 9.03
$C_{19}H_{32}O_4$.	Calculated %:	C 71.22; H 8.80
	Found:	M 329.1
	Calculated:	M 320.4 (by titration with NaOH)

with diazomethane. Hydrolysis of the cis lactone ester (XX) at the boil with excess of 30% caustic potash solution gave a good yield of the original cis lactone acid (XIX), m.p. 237-238°.

Action of Diazomethane on the cis Acid (IIIb)

A pure dry ethereal solution of diazomethane was added in slight excess, with cooling and stirring, to a suspension of 0.5 g of the cis acid (IIIb) in 25 ml of ether. After one hour at room temperature, ether was distilled off and the crystalline residue was boiled with 10 ml of petroleum ether; undissolved material was filtered off. The filtrate, when cooled, yielded 0.1 g of crystals, which were recrystallized from petroleum ether and then melted constantly at 89-90° and corresponded in composition to the cis diester (XXI).

	Found %:	C 73.02; 72.79; H 8.85; 8.85
$C_{21}H_{38}O_4$.	Calculated %:	C 72.79; H 8.72

The substance that was not dissolved by petroleum ether (0.4 g) was crystallized from a 2 : 1 mixture of ether and petroleum ether and yielded 0.35 g of pure cis lactone ester (XVII), m.p. 168-169°.

	Found %:	C 72.14; 72.40; H 8.22; 8.37
$C_{28}H_{22}O_4$.	Calculated %:	C 72.25; H 8.49

Hydrogenation of the cis Lactone Ester (XVII)

The cis lactone ester (XVII) (0.1 g; m.p. 168-169°) was dissolved in 5 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 9 ml (one molecular proportion) of hydrogen had been absorbed. The acetic acid was distilled off under reduced pressure, and the crystalline residue was recrystallized from 60% aqueous methanol. The product was 0.08 g of the cis lactone ester (XX), m.p. 175-176°, identical with that obtained previously by the action of diazomethane on the cis acid (XVI).

Hydrolysis of the cis Lactone Ester (XVII)

A mixture of 0.1 g of the cis lactone ester (XVII) and 3 ml of 30% caustic potash solution was boiled until solution was complete (six hours). Acidification precipitated a crystalline substance, and crystallization of this from 60% aqueous acetone yielded 0.07 g of pure cis lactone acid (XVIII), melting constantly at 243-244°.

	Found %:	C 71.56; 71.54; H 8.44; 8.46
$C_{19}H_{28}O_4$.	Calculated %:	C 71.56; H 8.23

Hydrogenation of 50 mg of this cis lactone acid in acetic acid in presence of a platinum catalyst and crystallization of the product from 60% aqueous acetone yielded 35 mg of the cis lactone acid (XIX), m.p. 238-239°, identical with the product obtained previously by the lactonization of the cis acid (XVI).

Hydrogenation of the cis Diester (XXI)

The cis diester (XXI) (80 mg; m.p. 90-91°) was dissolved in 3 ml of glacial acetic acid and hydrogenated over a platinum catalyst. One molecular proportion (6.5 ml) of hydrogen was absorbed. Crystals remaining after removal of acetic acid were recrystallized from petroleum ether, and yielded 60 mg of pure cis diester (XXII), melting constantly at 79-80°.

	Found %:	C 72.25; 72.37; H 9.24; 9.38
$C_{21}H_{32}O_4$.	Calculated %:	C 72.37; H 9.25

Displacement of the Double Bond in the cis Diester (XXI)

The cis diester (XXI) (0.1 g; m.p. 89-90°) was heated for one hour at 50° with 1 ml of a 1 : 1 mixture of acetic anhydride and glacial acetic acid saturated with dry hydrogen chloride. The liquid remaining after removal of solvents by distillation was dissolved in petroleum ether, and from this solution, when cooled with solid carbon dioxide, 60 mg of the isomeric cis diester (XXIII), m.p. 34-35°, separated.

	Found %:	C 72.48; H 9.01
$C_{21}H_{32}O_4$.	Calculated %:	C 72.37; H 9.25

Hydrogenation of the cis Acid (IIIc)

The cis acid (IIIc) (0.3 g; m.p. 203-204°) was dissolved in 10 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Only one molecular proportion of hydrogen was absorbed (39 ml at 20° and 740 mm). Acetic acid was distilled off, and the semisolid residue was hydrolyzed at the boil with 5 ml of 5% caustic soda solution. The resulting acid was recrystallized from 60% aqueous methanol, and 0.27 g of the cis acid (XXIV), m.p. 210-212° (dec.), was obtained.

cis Lactone Ester (XIII)

An ether suspension of 0.1 g of the cis lactone acid (XII) was treated with an ether solution of diazomethane. Ether was distilled off, and the reaction product was crystallized from petroleum ether. The product was 0.07 g of pure cis lactone ester (XIII) having a constant melting point of 145-146°.

	Found %:	C 71.87; 71.85; H 9.06; 9.04
$C_{24}H_{36}O_4$.	Calculated %:	C 71.81; H 9.04

The cis lactone ester (XIII), after prolonged boiling with excess of 10% sodium methoxide followed by hydrolysis, gave the original cis lactone acid (XII), m.p. 218-220°, in good yield.

Displacement of the Double Bond in the cis Diester (VIII)

A solution of 0.2 g of the cis diester (VIII) in 1 ml of a 1 : 1 mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. A liquid remained after removal of acetic acid and acetic anhydride under reduced pressure and this crystallized when treated with petroleum ether. Crystallization from petroleum ether gave 0.15 g of pure isomeric cis diester (XIV), m.p. 97-98°.

	Found %:	C 72.40; 72.45; H 8.98; 9.13
$C_{21}H_{32}O_4$.	Calculated %:	C 72.37; H 9.25

Hydrogenation of the cis Acid (IIIb)

a) The cis acid (IIIb) (1.0 g; m.p. 208-209°) was dissolved in 70 ml of glacial acetic acid and hydrogenated over a platinum catalyst. The volume of hydrogen absorbed was 124 ml (20°, 740 mm), corresponding to the hydrogenation of one double bond; no further hydrogenation occurred under these conditions. The catalyst was filtered off, solvent was distilled off under reduced pressure, and the nonhomogeneous crystalline product was hydrolyzed at the boil with 10 ml of 5% caustic soda solution. Acidification yielded 0.9 g of substance, and crystallization of this from 40% aqueous acetone yielded 0.5 g of pure cis acid (XIV), m.p. 218-219° (dec.).

	Found%:	C 71.20; 71.35; H 8.92; 8.74
$C_{19}H_{28}O_4$.	Calculated%:	C 71.22; H 8.80

b) In a similar way, 0.3 g of the cis acid (IIIb) was hydrogenated in 10 ml of glacial acetic acid. After removal of solvent the crystalline product was washed on the filter with petroleum ether and recrystallized from a 1 : 2 mixture of benzene and petroleum ether. The product was 0.15 g of pure cis anhydride (XV), m.p. 129-130°.

	Found %:	C 75.26; 75.17; H 8.93; 8.86
$C_{19}H_{24}O_3$.	Calculated %:	C 75.45; H 8.67

When hydrolyzed, this cis anhydride gave a good yield of the cis acid (XIV), m.p. 217-219° (dec.).

cis Lactone Acid (XIX)

A solution of 0.2 g of the cis acid (XVI), m.p. 218-219°, in 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. Acetic acid was distilled off under reduced pressure, and crystallization of the crystalline residue from 60% aqueous acetone yielded 0.15 g of the cis lactone acid (XIX), m.p. 238-239°.

	Found %:	C 71.15; 71.33; H 8.82; 8.70
$C_{19}H_{28}O_4$.	Calculated %:	C 71.22; H 8.80
	Found:	M 331
	Calculated:	M 320.4 (by titration with NaOH)

Action of Diazomethane on the cis Acid (XVI)

A suspension of 0.20 g of the cis acid (XVI) in ether was cooled and stirred while a slight excess of a dry purified ethereal solution of diazomethane was added. After one hour ether was removed under reduced pressure. Crystallization of the crystalline reaction product from a 3 : 1 mixture of diethyl ether and petroleum ether yielded 0.17 g of the cis lactone ester (XX), m.p. 175-176°.

	Found %:	C 71.63; 71.55; H 9.00; 9.05
$C_{24}H_{36}O_4$.	Calculated %:	C 71.81; H 9.04

The same cis lactone ester (XX) was obtained quantitatively when the cis lactone acid (XIX) was treated

Found %: C 71.29; 71.19; H 8.75; 8.86

$C_{19}H_{28}O_4$. Calculated %: C 71.22; H 8.80

The cis Diester (XXV), and its Isomerization into the cis Diester (XIV)

A suspension of 0.2 g of the cis acid (XXIV) in ether was treated with excess of an ether solution of diazomethane. After removal of ether the liquid cis diester (XXV) remained, and this did not solidify when treated with various solvents and when cooled. It was dissolved in 2 ml of a 1 : 1 mixture of acetic acid and acetic anhydride saturated with dry hydrogen chloride, and the solution was heated at 60° for one hour. Solvents were removed under reduced pressure, and the liquid product solidified when evaporated under reduced pressure with petroleum ether. Crystallization from petroleum ether yielded 0.1 g of an individual crystalline substance, m.p. 97-98°, and this was found to be identical with the cis diester (XIV), which was obtained previously as a result of double-bond migration in the cis diester (VIII).

SUMMARY

1. The condensation of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) with citraconic anhydride was studied, and all four theoretically possible stereoisomeric cis anhydrides (II; a, b, c, and d) were isolated. The structures of these, as ortho-addition products, were proved by dehydrogenation of the corresponding cis acids (III; a, b, c, and d) into 1,7-dimethylphenanthrene. No diene-synthesis products formed by para addition were detected.

2. When the isomeric cis acids (IIIa, IIIb, and IIIc) and their derivatives (anhydrides, diesters, lactone acids, and lactone esters) were hydrogenated in presence of a platinum catalyst, only one molecular proportion of hydrogen was absorbed —by reaction at the double bond in the ring A. Under these conditions the second double bond (in the ring C) was not hydrogenated. A peculiar feature in all of these hydrogenation reactions was their steric selectivity, which resulted in the formation of individual hydrogenated derivatives in which the 3- and 10-methyl groups always have a cis arrangement.

3. Isomerization of the cis diester (VII) with sodium methoxide yielded the trans acid (IX), which was hydrogenated to the trans acid (XI).

4. The isomeric cis acids (IIIa) and (IIIb), which were obtained in predominating amount, differ in the disposition of the substituents at C-5 and C-10, for double-bond migration in the diesters (VIII) and (XXII) yields different cis diesters (XIV) and (XXIII) having an inter-ring double bond. On the other hand, displacement of the double bond in the cis diester (VIII) and (XXV) gives, in each case, the same cis diester (XIV), so that the isomeric cis acids (IIIa) and (IIIc) differ only in the disposition of hydrogen at C-8.

5. The cis acids (IIIb) and (XVI), unlike the isomeric cis acids (IIIa) and (VI), are extremely prone to lactonization, and even when treated with diazomethane they give mainly the cis lactone esters (XVII) and (XX), instead of the corresponding diesters. This difference is in accord with their spatial structures: in the cis acid (IIIb), in which there is a trans arrangement of the 10-methyl and 13-carboxyl, the 10-methyl has no screening effect, and as a result lactonization is facilitated.

LITERATURE CITED

[1] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 78. (See Consultant's Bureau Translation, p 67).

[2] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 89.

[3] I. N. Nazarov and G. P. Kugatova, Bull. Acad. Sci. USSR, Divi Chem. Sci. 1955, No 3, 480. (See (Consultant's Bureau Translation, p 77).

[4] I. N. Nazarov, G. P. Verkholetova, L. V. Torgov, L. A. Zaretskaya, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 930, No. 6, 1074, (See Consultant's Bureau Translation, p955).

[5] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 1955, No. 2, 289. (See Consultant's Bureau Translation, p257).

[6] R. Haworth, B. Letsky, C. Mavin, J. Chem. Soc. 1932, 1789; R. Haworth et al., J. Chem. Soc. 1934, 459.

Received July 22, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

BLANK
PAGE

HIGH-TEMPERATURE REACTIONS OF METHYLCYCLOHEXANE IN A CONTINUOUS-FLOW SYSTEM IN PRESENCE OF METALS OF THE PALLADIUM GROUP AND OF HYDROGEN AT HIGH PRESSURE •

N. I. Shuikin, Kh. M. Minachev, L. M. Feofanova, E. G. Treshchova, T. P. Yudkina, and A. E. Agronomov

The reactions of hydrogenation, dehydrogenation, and aromatization of normal alkanes and the hydrogenolysis of cyclopentanes in presence of metals of Group VIII have been thoroughly studied [1-12]. These catalysts have a valuable selective action in many reactions, and wide use has been made of this peculiarity in the establishment of some of the general laws of heterogeneous catalysis. One theory of organic heterogeneous catalysis – the multiplet theory of Baladin – is largely based on experimental material obtained in the investigation of the specific properties of metal catalysts.

In recent years papers have appeared that relate to the application of platinum and nickel catalysts in the transformation of hydrocarbons at high temperature in presence of hydrogen at high pressure. Thus, in several papers [16-19] it is recommended that platinum should be applied on the industrial scale for the reforming of straight-run gasolines with the object of improving them as motor fuels, and the behavior, under these conditions, of some individual hydrocarbons is described.

Shuikin, Berdnikova, and Novikov [20, 21] investigated the catalytic reactions of several alicyclic hydrocarbons at 460° in presence of platinized alumina and hydrogen at 15-20 atm in a flow system. The results that they obtained are given in Table 1.

It will be seen from Table 1 that at high temperatures and in presence of hydrogen at high pressure the investigated cycloalkanes undergo various reactions with formation of a complex mixture of hydrocarbons. The mechanism proposed by the authors for these reactions was based on the methylene breakdown of some of the cycloalkane molecules and the methylation of the original hydrocarbon and its catalysis-reaction products by methylene radicals arising in this way. It must be pointed out that, already in 1934, Zelinsky and Shuikin [22] observed the formation of toluene, xylenes, and methyl- and dimethyl-cyclohexanes, with participation of methylene radicals, in the catalytic treatment of cyclohexane in presence of $Ni-Al_2O_3$ at 330-350°.

Ciapetta and Hunter [23] have investigated the reactions of normal alkanes, cyclopentanes, and cyclohexanes in presence of nickel, cobalt, iron, and platinum supported on various carriers at 250-480° in presence of hydrogen at high pressure in a flow system. The most active catalyst for the isomerization of normal alkanes was found to be 5% nickel on aluminosilicate.

Thus, the use of hydrogen at high pressure and temperatures of the order of 450° in the catalytic treatment of hydrocarbons of various classes in presence of metal-oxide catalysts results in the occurrence of reactions that occur either not at all or only to a slight extent when atmospheric pressure and temperatures not above 300-310° are used.

In the present paper we present new experimental material obtained in an investigation of the transformations of methylcyclohexane in contact with platinum, palladium, rhodium, and ruthenium catalysts. Alumina and silica gel were used as carriers. The properties of finely dispersed palladium at high temperatures and in presence of hydrogen at high pressure have received almost no study. The catalytic properties of rhodium and ruthenium in the reactions of hydrocarbons in general have been studied very little.

• The spectroscopic part of the work was carried out in the Molecular Spectroscopy Laboratory of the Chemistry Faculty of the Moscow State University under the supervision of V. M. Tatevsky, to whom the authors are grateful for help in assessing the results of the spectroscopic determinations.

TABLE 1

Compositions of Catalyzates Obtained as the Result of Reactions of Cyclopentane, Methylcyclopentane, and Cyclohexane in presence of Platinized Alumina Catalyst and of Hydrogen at High Pressure at 460°

Composition of catalysis products (% on original cycloalkane)	Original hydrocarbon		
	Cyclopentane	Methylcyclopentane	Cyclohexane
Degree of conversion	71.2	67.8	98.8
Gas and losses	22.6	8.3	6.6
Liquid catalyzate	77.4	91.7	93.4
Aromatic hydrocarbons	7.2	29.5	79.8
Cyclopentane	–	1.1	0.7
Methylcyclopentane	1.3	–	6.0
Pentane	34.5	3.1	2.6
2-Methylbutane	10.0	1.3	0.5
Other branched paraffins			
Those containing tertiary C	–	18.2	1.3
Those containing quaternary C	–	5.3	1.0
Unchanged cycloalkane	22.8	32.0	1.2
Not accounted for	1.6	1.2	0.3

EXPERIMENTAL

Carriers. Commercial silica gel was ground to particles of the size of 1.5-2.0 mm, treated several times with 1 : 1 hydrochloric acid, washed with distilled water until tests for chloride were negative, dried, and heated at 500° for three hours in a muffle. Alumina was first heated under the same conditions as the silica gel.

Catalysts. All catalysts were prepared under the same conditions. The carrier was impregnated with a dilute solution of H_2PtCl_6, $PdCl_2$, H_3RhCl_6, or $(NH_4)_2RuCl_5NO$ at room temperature, and then dried at 110° for 4-5 hours. It was then placed in the steel tube of an electric furnace and reduced with electrolytic hydrogen with gradual rise in temperature to 225-340°. The activity of the catalyst was determined by the extent of dehydrogenation of cyclohexane at 300-305°; with the exception of the ruthenium catalyst, all were extremely active.

Determination of the Specific Surfaces of Catalysts and Carriers. The specific surfaces of the catalysts and carriers were determined in an adsorption apparatus incorporating a McBain quartz-spring balance, adsorption isotherms being determined for benzene at 0°. The surfaces of the substances were first freed from adsorbed gases by exposure to a high vacuum (10^{-5} – 10^{-6} mm) at 250°. The distribution of pore size with respect to radius was calculated from the desorption branch of the isotherm with the aid of the Thomson-Kelvin formula [24],

$$RT \ln \frac{P_s}{P} = \frac{2\sigma V_m}{r},$$

($\frac{P}{P_s}$ is the relative pressure, σ is the surface tension of liquid benzene at 0°, V_m is the molar volume of liquid benzene, and r is the pore radius).

The results obtained are given in Table 2.

It follows from Table 2 that 1) the silica gel carrier has a greater specific surface and finer porous structure than the alumina; 2) the deposition of small amounts of metal on alumina does not generally affect the extent of the surface of this carrier, and the deposition of a similar amount of metal on silica gel always causes a slight increase in surface; 3) the deposition of metal on silica gel does not affect the position of the maximum on the curve for the distribution of pore size according to radius, but the deposition of some metals (Pd and Rh) on alumina causes an appreciable shift in the direction of smaller radii; 4) the total amount of benzene adsorbed on the surface at saturation is less on all of the catalysts investigated than on the corresponding carriers.

Methylcyclohexane. The methylcyclohexane used in the investigation was prepared by the hydrogenation of toluene in presence of Raney nickel at 180° in an autoclave. After necessary purification it had b.p. 99.8-100.6° (corrected), n_D^{20} 1.4230, and d_4^{20} 0.7693.

TABLE 2

Specific Surfaces of Catalysts and Carriers

Catalyst or carrier	Specific surface (sq.m/g)	Position of maximum pore size on size-distribution curve (A)	Range of pore radii (A)	Total amount of adsorbed benzene at $\frac{P}{P_s}$ = 1 (millimoles/g)
SiO_2, clear.	195	15 and 31	12 – 32	4.50
SiO_2, translucent. . .	195	14	11 – 18	3.20
0.5% Pt – SiO_2	220	15	11 – 18	3.70
0.5% Pd – SiO_2	220	15	12 – 24	3.70
1.0% Ru – SiO_2	220	14	11 – 20	3.25
0.5% Rh – SiO_2. . . .	220	15	12 – 20	3.55
Al_2O_3.	90	42	20	5.80
0.5% Pt – Al_2O_3. . . .	70	43	18	5.10
0.5% Pd – Al_2O_3. . . .	90	32	18	5.10
1.0% Ru – Al_2O_3. . . .	90	39	18	5.50
0.5% Rh – Al_2O_3. . . .	85	35	18	5.25

TABLE 3

Properties of Methylcyclohexane Catalyzates Obtained in Experiments with Different Catalysts

Catalyst	Amount of substance taken (g)	Amount of catalyzate obtained (g)	Gas and losses		Properties of catalyzate			Composition of gas (%)	
			(g)	(%)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (toluene) (%)	H_2	C_nH_{2n+2}
Pt – Al_2O_3	154.0	145.6	8.6	5.5	1.4820	0.8467	82.1	100	–
Pd – Al_2O_3	224.2	214.3	9.9	4.4	1.4820	0.8466	82.1	100	–
Rh – Al_2O_3	153.0	148.6	5.3	3.4	1.4537	0.8090	47.0	100	–
Ru – Al_2O_3	166.2	141.3	25.0	15.1	1.4425	0.7940	25.0	87	13
Pt – SiO_2	231.0	209.9	21.1	8.7	1.4937	0.8623	96.3	100	–
Pd – SiO_2	228.1	211.2	17.0	7.4	1.4910	0.8601	93.0	100	–
Rh – SiO_2	349.3	250.4	99.0	28.3	1.4620	0.8210	57.7	67.6	22.4
Ru – SiO_2	307.8	169.2	138.6	45.0	1.4264	0.7723	5.3	47.5	52.5

Apparatus and Procedure. The apparatus is described in a previous communication [25]. The experiments were carried out at 460° in presence of hydrogen at 20 atm pressure at a space velocity of 1.1 liters of methylcyclohexane per liter of catalyst, the ratio of hydrocarbon to hydrogen being 1 : 5. In addition, experiments with platinized alumina were carried out at 35 and 50 atm. The volume of catalyst was 50 ml in all experiments.

Investigation of Catalyzates. The methylcyclohexane catalyzates were investigated by the methods of precise rectification, chromatographic adsorption, and Raman spectra. Gaseous products were analyzed in an Orsat-Lunge apparatus.

The properties of the methylcyclohexane catalyzates obtained with various catalysts are given in Table 3, from which it can be seen that platinum and palladium, both on alumina and on silica, are extremely active catalysts for the reactions of methylcyclohexane. The least active catalyst is ruthenium on a silica carrier. The values given in Table 3 for the toluene contents (% by weight) of the catalyzates were determined from the data of Lozovoi and coworkers [26].

Aromatic hydrocarbons, which were separated from the catalyzates by adsorption on silica gel, were fractionated through a 33-plate column. Their fractional compositions and properties are given in Table 4.

The data in Table 4 show that the main direction of the transformations of methylcyclohexane under the given conditions is dehydrogenation to toluene. However, in addition to toluene, benzene and xylene were always found in the aromatic part of the catalyzate. From the catalyzate obtained in presence of rhodium on silica gel, 32.3% of benzene was isolated. Some fractions having boiling points below and above that of toluene were analyzed with the aid of Raman spectra. In the experiments with Pt – Al_2O_3, Pt – SiO_2, Pd – Al_2O_3, Pd – SiO_2, Rh – Al_2O_3

and Rh – SiO_2, the catalyzates contained small amounts (0.5-2.0%) of xylene. In the catalyzates obtained in presence of Pd – Al_2O_3, Pd – SiO_2, Pt – SiO_2 and Ru – SiO_2, 1.2-5% of benzene was found. Under the given conditions, therefore, demethylation and methylation processes occur.

TABLE 4

Fractional Composition and Properties of Aromatic Hydrocarbons Isolated from Methylcyclohexane Catalyzates

Catalyst	Amount of aromatic hydrocarbons taken for fractionation (g)	Fraction	Properties of fractions			Weight of fraction (g)	Yield (% by weight)	
			Boiling range (°C)	n_D^{20}	d_4^{20}		on mixture taken	on original methylcyclohexane
Pt – Al_2O_3	107.4	I	105 – 109.6	1.4950	0.8648	0.8	0.74	
		II	109.6–110	1.4968	0.8662	100.3	93.3	68.2
		III	110 – 126	1.4973	0.8669	4.5	4.2	
			Residue			1.6	1.5	
Pd – Al_2O_3	156.0	I	104 – 109.7	1.4960	0.8646	3.5	2.2	
		II	109.7–110.8	1.4958	0.8667	146.3	93.6	68.7
		III	110.8–124	1.4969	0.8671	4.2	2.7	
			Residue			2.0	1.3	
Rh – Al_2O_3	40.7	I	107.5 – 109.5	1.4940	0.8629	0.6	1.4	
		II	109.5–110.6	1.4970	0.8676	35.5	85.8	25.1
		III	110.6–118	1.4970	0.8666	3.6	8.85	
			Residue			1.0	2.4	
Ru – Al_2O_3	31.2	I	106.5–109	1.4675	–	0.86	2.8	
		II	109 – 110	1.4960	0.8660	26.2	84.0	17.5
		III	110–110.5	1.4970	0.8663	2.5	8.0	
			Residue			1.7	–	
Pt – SiO_2	177.5	I	104 – 109	1.4980	0.8685	4.2	2.4	
		II	109–110.5	1.4965	0.8684	168.0	94.7	75.9
		III	110.5–125	1.4990	0.8698	3.0	1.7	
			Residue			2.3	1.3	
Pd – SiO_2	167.0	I	100 – 109	1.4940	0.8581	3.6	2.1	
		II	109 – 110	1.4955	0.8664	156.9	94.0	72.3
		III	110 – 115	1.4970	0.8669	4.3	2.6	
			Residue			2.2	1.3	
Rh – SiO_2	80.0	I	76.5 – 79.5	1.4860	–	0.8	1.0	
		II	79.5 – 79.7	1.4995	0.8750	25.8	32.3	
		III	79.7 – 109	1.4970	0.8668	1.4	1.75	22.3
		IV	109 – 110	1.4960	0.8655	45.0	56.3	
		V	110 – 130	1.5005	0.8713	3.3	4.1	
			Residue			1.6	2.0	
Ru – SiO_2	6.9		95 – 113°	1.4950	0.8649	6.5	94.2	2.1
			Residue			0.4	5.8	

The fractional composition and properties of the naphthene part of the methylcyclohexane catalyzate, which remains after chromatographic separation of the aromatic hydrocarbons, are shown in Table 5, from which it will be seen that the boiling points and other properties of the hydrocarbons isolated are considerably different from those of the original methylcyclohexane. In order to determine the composition of the mixture of hydrocarbons obtained we usedthe Raman-spectra method. The results of this investigation are given in Table 6, which shows that the main products of the transformations of methylcyclohexane are 1,2- and 1,3-dimethylcyclopentanes. In the presence of Pt – Al_2O_3 and of Pd – Al_2O_3 the main product of the transformations of methylcyclohexane is trans-1,2-dimethylcyclopentane. In presence of Rh – Al_2O_3 and Ru – Al_2O_3, in addition to 1,2-dimethylcyclopentane, appreciable amounts of 1,3-dimethylcyclopentane are formed in cis and trans forms. Also, a small amount of cyclohexane is present in almost all of the catalyzates.

TABLE 5

Fractional Composition and Properties of the Naphthene Parts of Methylcyclohexane Catalyzates

Catalyst	Amount of catalyst taken for fractionation (g)	Fraction	Properties of fractions			Weight of fraction (g)	Yield (% by weight)		
			Boiling range (°C)	n_D^{20}	d_4^{20}		on mixture taken	on catalyzate	on original methylcyclohexane
$Pt-Al_2O_3$	20.8	I	87–98	1.4168	0.7570	4.5	21.6	3.1	1.9
		II	98–100.5	1.4230	0.7688	8.6	41.4	5.9	5.6
		III	98–100.9	1.4233	0.7689	6.3	30.3	4.3	4.1
		Residue	–	–	–	1.4	6.7	–	–
$Pd-Al_2O_3$	44.5	I	85–98	1.4163	0.7564	5.5	12.3	2.6	2.5
		II	98–100.5	1.4230	0.7691	26.1	58.0	12.2	11.6
		III	98–100.5	1.4230	0.7690	10.4	24.5	4.9	4.6
		Residue	–	–	–	2.5	5.6	1.2	1.1
$Rh-Al_2O_3$	22.1	I	81–95	1.4110	0.7476	11.0	50.0	7.4	7.2
		II	95–100	1.4203	0.7624	4.2	19.1	2.8	2.7
		III	100–101	1.4235	0.7691	5.7	24.1	3.9	3.7
		Residue	–	–	–	1.2	5.5	0.8	0.3
$Ru-Al_2O_3$	69.0	I	84.5–91.0	1.4112	0.7482	10.0	14.5	7.1	6.0
		II	91.0–99.5	1.4200	0.7622	3.8	5.7	2.7	2.3
		III	99.5–100.5	1.4233	0.7693	46.4	67.3	32.9	28.0
		IV	100.5–103.0	1.4235	0.7702	6.3	9.2	4.5	3.8
		Residue	–	–	–	2.3	3.3	1.6	1.4
$Pt-SiO_2$	2.8	I	91.3–100.4	1.4186	0.7580	2.6	93.0	1.3	1.1
$Pd-SiO_2$	3.8	I	93–100.2	1.4190	0.7640	3.5	92.2	1.7	1.5
$Rh-SiO_2$	86.6	I	42–99.5	1.4155	0.7345	4.85	5.6	1.9	1.4
		II	99–100.5	1.4232	0.7697	70.0	81.0	28.0	20.1
		III	100.5–102.0	1.4235	0.7695	10.8	12.5	4.3	3.1
		Residue	–	–	–	1.0	1.2	0.4	0.3
$Ru-SiO_2$	161.5	I	95.6–99.5	1.4213	0.7643	10.0	6.2	5.9	3.3
		II	99.5–100.4	1.4232	0.7695	137.8	85.0	81.7	44.8
		III	100.4–103	1.4235	0.7696	9.2	5.7	5.5	3.0
		Residue	–	–	–	4.5	2.8	2.7	1.5

Transformations of Methylcyclohexane in presence of Alumina and Silica

In connection with these results it was of interest to determine the behavior of methylcyclohexane in presence of pure alumina and pure silica, such as we had used as carriers in the preparation of the catalysts. With this object we carried out catalysis experiments with methylcyclohexane over silica and over alumina in presence of hydrogen at 20, 35, and 50 atm, other experimental conditions being identical with those described above.

Analysis of the resulting catalyzates showed that under the given conditions both silica gel and alumina promote partial isomerization of methylcyclohexane into trans- and cis-1,2-dimethylcyclopentanes; with silica gel, however, this process occurs already at 20 atm, whereas with alumina isomerization is not appreciable until 50 atm is reached. Traces of cyclohexane were also found in the catalyzates, which points to partial demethylation of the original methylcyclohexane. It appears that cleavage of methylcyclohexane and its isomerization products does not occur in this case. Also, no aromatic hydrocarbons were detected in the catalyzates.

Effect of the Pressure of Hydrogen on the Degree of Conversion of Methylcyclohexane

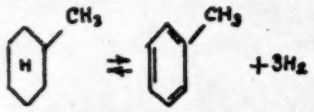
It was important to investigate in further experiments the effect of the pressure of hydrogen on the reactions of methylcyclohexane, other conditions being kept as before. The catalyst selected for this purpose was platinized alumina. We had already carried out experiments at 20 atm, and we now supplemented these by experiments at 35 and 50 atm.

TABLE 6

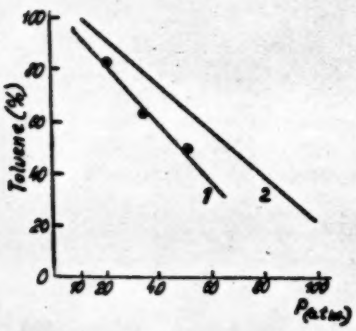
Results of the Optical Investigation of Methylcyclohexane Catalyzates

Catalyst	Fraction (see Table 5)	Composition (%)						
		trans-1,2-dimethyl-cyclopentane	cis-1,2-dimethyl-cyclopentane	trans-1,3-dimethyl-cyclopentane	cis-1,3-dimethyl-cyclopentane	cyclohexane	methylcyclohexane	cyclopentane
$Pt-Al_2O_3$	I	17–20	–	–	–	1.0–1.5	82–80	–
	II	6–7	–	–	–	–	94–93	–
	III	0.5	–	–	–	–	99.5	–
$Pd-Al_2O_3$	I	20–22	–	–	–	3	70–75	–
	II	8–10	–	–	–	–	90–92	–
	III	8–10	–	–	–	–	90–92	–
$Rh-Al_2O_3$	I	30	–	22	46	–	2–3	–
	II	23–20	–	–	–	–	77–80	–
	III	1	–	–	–	–	99	–
$Ru-Al_2O_3$	I	28	–	32	40	–	traces	–
	II	25	5	25	40	–	5	–
	IV	7–10	–	–	traces	traces	90–93	–
$Rh-SiO_2$	I	–	–	–	–	3.5	94	2.5
$Ru-SiO_2$	I	–	–	–	–	2–3	97	–

The graph gives the dependence of the yield of toluene on the pressure of hydrogen for a temperature of 460°, and also the yields of toluene calculated from Vvedensky's data [27] for the equilibrium concentrations in the following reaction at the same temperature: methylcyclohexane $\rightleftarrows$ toluene + hydrogen. At 50 atm the experimental values differ from the calculated values by 17 – 18%, whereas at lower pressures this difference falls to 8-5%. These discrepancies are to be explained by the fact that at higher pressure the reaction



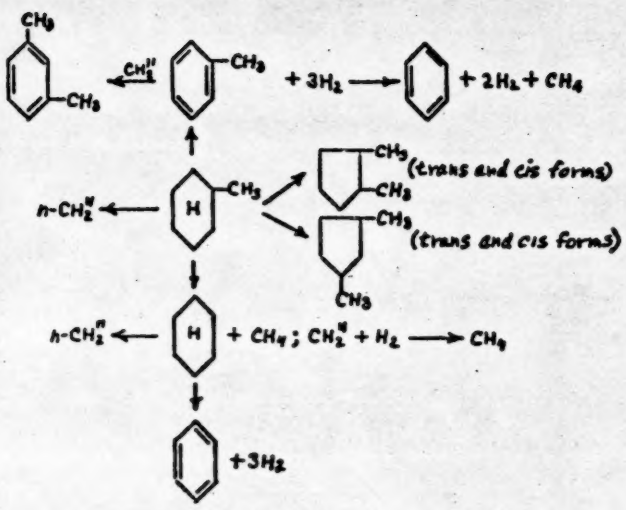
does not attain equilibrium owing to simultaneous isomerization of the methylcyclohexane into dimethylcyclopentanes. Optical analysis of fractions of the catalyzate shows that they contain more than 10% of dimethylcyclopentanes (on the original methylcyclohexane). Analysis of the aromatic hydrocarbons obtained showed that they consisted mainly of toluene, though 1-2% of m-xylene was present in the fraction boiling above 110°.



Dependence of the yield of toluene on the pressure of hydrogen (in experiments at 460°): 1-experimental data; 2-from equilibrium concentrations.

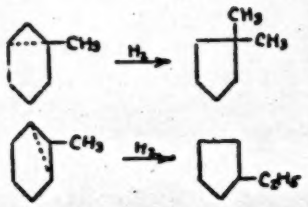
The experimental material that we have obtained relating to the transformations of methylcyclohexane in presence of platinum, palladium, rhodium, and ruthenium deposited on alumina and silica shows that this hydrocarbon undergoes various far-reaching changes under the given conditions. The reactions that occur may be

expressed as follows:



The main reaction of methylcyclohexane under the given conditions is its dehydrogenation to toluene. The amounts of benzene and xylenes present in the catalyzates are very small. Only in experiments with the rhodium-silica catalyst was there a considerable amount of benzene (32%) in the aromatic part of the catalyzate. Under the given conditions, therefore, the processes of demethylation and methylation of the benzene nucleus occur, with participation of methylene radicals [20-22]. Under our conditions the source of methylene radicals may be the methylene breakdown of the original methylcyclohexane and of other cycloalkanes formed from it by hydrogenolysis of the side group (cyclohexane) or by isomerization with contraction of the ring (dimethylcyclopentanes).

Another important reaction is the isomerization of methylcyclohexane into dimethylcyclopentanes. In the catalyzates we found 1,2- and 1,3-dimethylcyclopentanes. With one exception ($Pt-Al_2O_3$ at 35 atm) we could not detect the presence of 1,1-dimethylcyclopentane and ethylcyclopentane in the catalyzates, although these substances could be formed from methylcyclohexane by ring contraction according to the scheme:



However, in the catalysis experiment on methylcyclohexane in presence of $Pt-Al_2O_3$ at 460° and 35 atm we detected the presence of about 34% of 1,1-dimethylcyclopentane in the 86-90° fraction of the catalyzate by the optical method (Table 7). We intend to investigate this interesting observation in greater detail in the future.

It is interesting that under the given conditions in presence of silica gel or alumina methylcylcohexane undergoes partial isomerization to dimethylcyclopentanes. The literature shows that at 450° in absence of pressure, neither over alumina [28, 29] nor over silica [28] does the cyclohexane ring suffer any appreciable change. Under the same conditions cyclohexene and 4-methylcyclohexene are isomerized in presence of alumina [28] and of silica [28] into the corresponding dimethylcyclopentenes.

In 1943 Haensel and Ipatieff [80] in a study of the reactions of cyclohexane over alumina at 570-578° in presence of hydrogen at 100 atm in a flow system, showed that under these conditions cyclohexane is partially isomerized into methylcyclopentane. A similar observation was made earlier by Ipatyev (Ipatieff) and Dovgelevich [29]. With respect to the dehydrogenation of methylcyclohexane, platinum and palladium had practically

the same, high activity under the given conditions; rhodium was more active than ruthenium. Platinum, palladium, and rhodium were more active when carried by silica gel than when carried by alumina. Ruthenium, on the other hand, was more active on alumina. The most active catalysts in effecting the far-reaching breakdown of the hydrocarbons were ruthenium and rhodium on silica gel. The properties of platinum and palladium catalysts were not greatly dependent on the identity of the carrier, but those of the ruthenium and rhodium catalysts were. When these were deposited on silica gel they promoted considerable cleavage, both of the original hydrocarbon and of the products of its transformation. This behavior may be determined in part by the specific surfaces of the carriers (see above).

TABLE 7

Composition and Properties of the Naphthene Part of the Methylcyclohexane Catalyzate obtained over $Pt-Al_2O_3$

Pressure of hydrogen (atm)	Amount of substance (g)	Fraction	Properties			Weight (g)	Yield (% on original methylcyclopentane)	Composition according to optical analysis (%)					
			Boiling range (°C)	n_D^{20}	d_4^{20}			trans-1,2-dimethylcyclopentane	cis-1,2-dimethylcyclopentane	trans-1,3-dimethylcyclopentane	cis-1,3-dimethylcyclopentane	methylcyclopentane	cyclohexane
35	57.2	I	86-90	1.4085	0.7404	3.8	2.2	30	34*	22	11	–	3
		II	90-95	1.4115	0.7464	4.4	2.8	60	15	12	8	4	–
		III	95-100	1.4205	0.7639	4.1	2.5	25	Traces			75	–
		IV	100-100.2	1.4235	0.7695	34.3	21.4	Not investigated					
		V	100.2-102	1.4235	0.7698	9.6	6.3	Not investigated					
		Residue		–	–	0.4							
50	65	I	84-90	1.4113	0.7451	6.6	4.6	25	8	22	45	–	–
		II	90-95	1.4123	0.7488	7.1	5.0	30	–	22	46	2	–
		III	95-99	1.4213	0.7646	6.1	4.3	Traces	–	–	–	100	–
		IV	99-99.5	1.4230	0.7694	38.8	27.3	Not investigated					
		V	99.5-102.0	1.4235	0.7695	3.1	2.2	Traces	–	–	–	100	–
		Residue		–	–	2.7							

*1,1-Dimethylcyclopentane

SUMMARY

1. An investigation was made of the catalytic properties of finely dispersed platinum, palladium, rhodium, and ruthenium deposited on alumina and on silica gel in the transformations of methylcyclohexane at 460° in presence of hydrogen at 20, 35, and 50 atm in a flow system.

2. It was shown that at 460° and in presence of hydrogen at 20 atm the main reaction of methylcyclohexane is dehydrogenation to toluene. The extent of the dehydrogenation of the original hydrocarbon depends both on the nature of the metal and on the chemical nature of the carrier.

3. It was shown that under the given conditions dehydrogenation is accompanied by isomerization processes with formation of isomeric dimethylcyclopentanes and also by the demethylation and methylation of hydrocarbons with participation of methylene radicals.

4. With increase in pressure, other conditions being maintained constant, there is an increase also in the extent to which methylcyclohexane undergoes isomerization with contraction of the ring.

5. Study of the behavior of methylcyclohexane in contact with silica and alumina showed that these oxides promote partial isomerization of the original hydrocarbon into dimethylcyclopentanes.

LITERATURE CITED

[1] N. D. Zelinsky, Selected Works, Vol. I and II, Acad. Sci. USSR Press, Moscow and Leningrad, 1941.

[2] S. Yu. Elovich and G. M. Zhabrova. Theoretical Principles of the Hydrogenation of Fats, Acad. Sci. USSR Press, Moscow, 1948.

[3] S. N. Obryadchikov, Petroleum Technology. Part 2. Moscow and Leningrad, 1952, p. 305.

[4] A. M. Rubinshtein, Kh. M. Minachev, and N. I. Shuikin. Proc. Acad. Sci. USSR, 62, 497 (1948); 67, 287 (1949).

[5] N. I. Shuikin, Kh. M. Minachev, and A. M. Rubinshtein, Proc. Acad. Sci. USSR, 79, 89 (1951).

[6] Kh. M. Minachev and N. I. Shuikin, Proc. Acad. Sci. USSR, 72, 61 (1950).

[7] B. A. Kazansky and A. F. Plate, J. Gen. Chem. 7, 328 (1937).

[8] B. A. Kazansky and A. F. Plate, J. Gen. Chem. 9, 496 (1939).

[9] B. A. Kazansky, A. L. Liberman, and M. I. Batuev, Proc. Acad. Sci. USSR 41, 67(1948).

[10] A. F. Plate, Catalytic Aromatization of Paraffins, Acad. Sci. USSR Press, Moscow and Leningrad, 1948.

[11] N. D. Zelinsky, B. A. Kazansky, and A. F. Plate, Ber. 68, 1869 (1936).

[12] B. A. Kazansky, Prog. Chem. 17, 641 (1948).

[13] N. D. Zelinsky and A. A. Balandin, Bull. Acad. Sci. USSR 7, 29 (1929).

[14] A. A. Balandin Z. phys. Chem. 3, 167, 1929; ibid 4, 289 (1929).

[15] A. A. Balandin, Jubilee Collection, dedicated to the Thirtieth Anniversary of the Great October Socialist Revolution, Moscow and Leningrad, 1947, p. 627.

[16] V. Haensel, Oil and Gas J. 48, 82 (1950).

[17] V. Haensel, Petr. Process 5, 356 (1950).

[18] M. L. Kastens and R. E. Sutherland, Ind. Eng. Chem. 42, 582 (1950).

[19] V. Haensel and G. R. Donaldson, Ind. Eng. Chem. 43, 2102 (1951).

[20] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 269.*

[21] N. I. Shuikin, S. S. Novikov, and N. G. Berdnikova, Proc. Acad. Sci. USSR 89, 1029 (1953).

[22] N. D. Zelinsky and N. I. Shuikin, Proc. Acad. Sci. USSR 3, No. 4, 255 (1934).

[23] F. G. Ciapetta and I. B. Hunter, Ind. Eng. Chem. 45, 147 (1953).

[24] I. W. McBain, A. M. Baker, J. Am. Chem. Soc. 48, 690 (1926); A. V. Kiselev, Prog. Chem. 14, 367 (1945).

[25] Kh. M. Minachev, N. I. Shuikin, L. M. Feofanova, T. G. Treshchova and T. P. Yudkina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 1067.

[26] A. V. Lozovoi, M. K. Dyakova, and T. G. Stepantseva, J. Gen. Chem. 7, 1119 (1937); A. A. Balandin and N. I. Shuikin, J. Phys. Chem. 5, 707 (1934).

[27] A. A. Vvedensky, Thermodynamical Calculations for Processes of the Fuel Industry, State Fuel Tech. Press, Leningrad and Moscow, 1949.

[28] Yu. A. Arbuzov, Sci. Mem. Moscow State Univ. 89, 70 (1945).

[29] V. N. Ipatyev and P. Dovgelevich, J. Russ. Phys. Chem. Soc. 43, 1431 (1911).

[30] V. Haensel and V. N. Ipatieff, Ind. Eng. Chem. 35, 632 (1943).

Received May 12, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

* Consultant's Bureau Translation, p 243.

BLANK
PAGE

DESTRUCTIVE ALKYLATION OF BENZENE WITH PENTANE

I. M. Tolchinsky, B. A. Krentsel, and A. V. Topchiev

Investigation of the thermal and catalytic processes occurring in the transformations of pure hydrocarbons and mixtures of hydrocarbons under various conditions is of undoubted interest for the extension of our ideas concerning the chemistry and mechanisms of the complex reactions occurring in thermocatalytic treatments of petroleum. Not only the many thermocatalytic transformations of hydrocarbons, but also the destructive alkylation of aromatic hydrocarbons with paraffins is deserving of attention. As is well known, in this process cracking of the paraffin molecule is associated with the simultaneous addition of the resulting unsaturated hydrocarbon to the thermally more stable molecule of benzene or other aromatic hydrocarbon.

The general equation for the destructive alkylation of aromatic hydrocarbons with paraffins is as follows:

$$C_{(m+n)}H_{2(m+n)+2} + ArH \longrightarrow C_nH_{2n+2} + ArC_mH_{2m+1}$$

In the literature various catalysts have been proposed for the destructive alkylation of aromatic hydrocarbons. In the alkylation of benzene with 2,2,4-trimethylpentane [1] the following catalysts were tried: aluminum chloride, zirconium chloride, boron trifluoride, and magnesium chloride. Aluminum and zirconium chlorides were active catalysts; in presence of boron trifluoride and magnesium chloride the reaction did not go. The product of the reaction was tert-butylbenzene, and the further alkylation of this yield di-tert-butylbenzene.

Other authors have investigated the destructive alkylation of benzene with hexane and with 2,2,4-trimethylpentane in presence of orthophosphoric acid [2]. The amount of catalyst taken was about 20% of the total amount of reactants. Treatment of a mixture of benzene and hexane at 450° for ten hours in a revolving autoclave gave a yield of liquid reaction products amounting to 84% of the weight of starting materials, and the gas formed amounted to 6 liters from every 100 g of reacting hydrocarbons. The liquid products contained 2.8% of isopropylbenzene and 7.1% of butylbenzenes, the remainder being unchanged benzene and hexane. The gas contained 54% of ethane, 28% of hydrogen, and 18% of propane. In the reaction with 2,2,4-trimethylpentane tert-butylbenzene was formed, as in the experiment in presence of aluminum chloride; the gaseous products contained 63.2% of isobutane.

In a patent [3] it is proposed to carry out the alkylation of aromatic hydrocarbons by means of paraffins in presence of an aluminosilicate catalyst at about 450°. No information is given about the conditions of the process and the composition of the products.

The literature on the reaction of paraffins with benzene is therefore almost entirely concerned with the investigation of reactions occurring in presence of metal chlorides and phosphoric acid. It was considered to be of interest to study the reactions of benzene with the lower paraffins in presence of a technical aluminosilicate catalyst under conditions close to those that we used previously in our investigations of the thermal transformations of pentane [4].

EXPERIMENTAL

The starting materials were a pentane fraction obtained by the rectification of a light straight-run gasoline and commercial benzene, which was distilled and collected within a range of 1°. The characteristics of these materials are given in Table 1.

The reactions were carried out in a 500-ml rotating autoclave. The procedure was the same as that used in the investigation of the transformations of pentane [4]. The liquid reaction products were fractionated, the fractions collected being: up to 60°, 60-95°, 95-122°, 122-150°, 150-200°, and above 200°. The fractions boiling above 95° were regarded as the actual reaction products. These fractions were then subjected to precise rectification through a column having a metal packing and equivalent in resolving power to fifty theoretical plates. The narrow fractions obtained by precise rectification were characterized by the usual physicochemical properties, and some of them were investigated with the aid of their Raman spectra. In experiments directed to the study

of the overall balance sheet of the reaction, the gaseous products were collected and analyzed in a low-temperature rectification apparatus.

TABLE 1

Characteristics of Starting Materials

Substance	d_4^{20}	n_D^{20}	Boiling range	Bromine number
Pentane	0.6297	1.3579	34-36.3	0
Benzene	0.8798	1.5009	79-80	–

Effect of Temperature, Duration of Reaction, and Amount of Catalyst on the Yield of Products formed in the Reaction of Pentane with Benzene

a) Effect of Temperature. Experiments to determine the effect of temperature on the yields of products were carried out with equimolecular amounts of benzene and pentane; the duration of reaction was 120 minutes, and the amount of catalyst (commercial aluminosilicate catalyst in spherical granules) was 23-25% on the weight of reacting hydrocarbons. The results of typical experiments of this series are given in Table 2.

Analysis of the results in Table 2, which are represented graphically in Fig. 1, shows that, as the temperature is raised, the yield of gas increases at the expense of a reduction in the amount of liquid reaction products. This conclusion is in accord with results that we obtained in a study of the autodestructive alkylation of pentane over an aluminosilicate catalyst. Control experiments carried out under the same conditions with benzene alone (no pentane) showed that benzene underwent no appreciable change. In view of the above considerations, it is not advisable to carry out the reaction at above 450-460°.

TABLE 2

Effect of Temperature on the Yields of Products of the Destructives Alkylation of Benzene with Pentane

Amount taken (g)		Experimental conditions				Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of liquid reaction products
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)		gas	liquid	coke + losses	on liquid product	on starting materials	
		maximum	average	maximum	average						
122	113	450	455	520	425	22.7	66.5	10.8	56.0	31.7	0.7573
137	126	440	435	570	530	13.0	65.0	22.0	44.7	29.2	0.7836
137	126	425	420	430	420	3.8	80.5	15.7	35.4	28.6	0.7568
145	133	398	390	530	515	0.36	88.5	11.14	9.35	8.3	0.7460

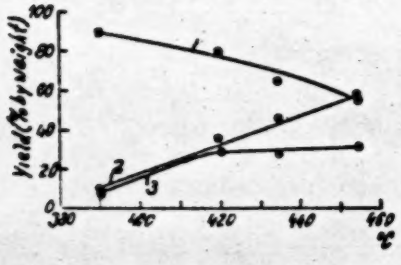


Fig. 1 (based on Table 2). The effect of temperature on the yield of liquid products of the alkylation of benzene with pentane (duration of experiment 120 minutes; amount of catalyst 23.5-26.6% by weight).
Curve 1 - The whole liquid product; Curve 2 - fraction boiling above 95°, calculated on liquid product; Curve 3 - fraction boiling above 95°, calculated on starting materials.

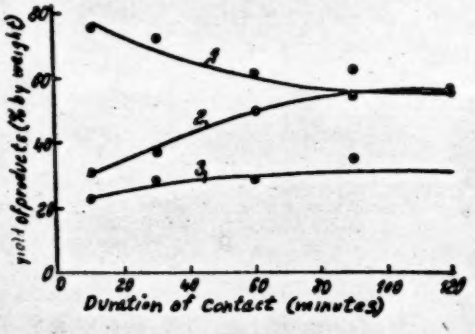


Fig. 2. (based on Table 3). The effect of duration of contact on the yield of liquid products of the destructive alkylation of benzene with pentane.
Curve 1 - The whole liquid product; Curve 2 - fraction boiling above 95°, calculated on the starting materials; Curve 3 - fraction boiling above 95°, calculated on the liquid.

b) Effect of the Duration of Reaction. The experiments on the effect of the duration of reaction on the yields of the products of the reaction of benzene with pentane were carried out with the same amounts of reactants and catalyst. The results are given in Table 3 and are represented graphically in Fig. 2.

Analysis of the results in Table 3 shows that increase in the duration of the reaction to more than 60 minutes does not lead to an appreciable increase in the yield of products boiling above 95°, i.e. products of the interaction of benzene and pentane.

c) Effect of the Amount of Catalyst. Experiments to determine the effect of the amount of catalyst were carried out at about 450° for a contact time of 10 minutes. The results given in Table 4 show that increase in the amount of catalyst to above 12% (on the reactants) had almost no effect, over the investigated range, on the yields of gas and liquid reaction products.

TABLE 3

Effect of Duration of Contact on the Yields of the Products of the Destructive Alkylation of Benzene with Pentane

Amount taken (g)		Experimental conditions				Duration of reaction (in minutes)	Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of crude product
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)			gas	liquid	coke + losses	on liquid product	on starting materials	
		maximum	average	maximum	average							
127	118	465	462	490	480	10	6.5	75.5	18	30.3	22.9	0.7644
124	115	460	455	490	445	30	12.2	72.3	15.5	38.3	27.8	0.8019
119	111	460	455	518	459	60	18.3	61.0	20.7	49.4	30.0	0.8267
118	109	460	455	448	380	90	16.8	62.5	20.9	55.5	34.8	–
122	113	460	455	520	425	120	22.7	56.5	20.8	56.0	31.7	0.7573

TABLE 4

Effect of Amount of Catalyst on the Yields of Products

Amount taken (g)		Experimental conditions				Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of reaction products	Amount of catalyst (% by weight on reactants)
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)		gas	liquid	coke	on liquid product	on starting materials		
		maximum	average	maximum	average							
115	108	470	465	440	418	9.65	61.5	29.0	32.8	20.2	0.7718	58.8
124	116	470	468	555	522	7.3	69.0	24.0	35.0	24.2	0.7727	45.8
132	123	465	462	535	525	7.0	75.5	18.5	28.6	21.6	0.7660	26.3
127	118	465	462	425	425	5.8	84.3	9.7	27.5	23.2	0.7729	14.3
135	125	465	462	530	520	6.4	82.8	10.9	28.0	23.1	0.7655	12.7
137	128	470	460	490	457	6.1	86.8	7.15	10.45	9.05	0.7603	0.0
119•	111	470	460	490	395	21.4	63.0	15.5	20.7	13.0	0.8549	0.0

• Duration of contact 120 minutes.

However, in absence of catalyst reaction proceeds with a considerably lower yield of liquid product. Results given in this table are represented also in Fig. 3.

Investigation of Liquid Reaction Products obtained in the Reaction of Pentane with Benzene

The amount of liquid products taken for investigation was 2000 ml (it had been previously distilled, to remove unchanged pentane, from a flask fitted with a dephlegmator), and this was fractionated through a column of high productivity (the load in the flask was 2000 ml) having a metal packing equivalent in resolvability to thirty theoretical plates. The following wide fractions were obtained:

Frac. I,	up to	40°;	114 ml;	5.7%
Frac. II,	b.p.	40-95°;	1173 ml;	58.4%
Frac. III,	b.p.	95-200°;	570 ml;	28.7%
Frac. IV,	b.p.	> 200°;	63 ml;	3.2%
		Losses —	80 ml;	4.0%

Fraction I, which came over below 40°, had the following characteristics: d_4^{20} 0.6301; n_D^{20} 1.3587, bromine number 0, amount of sulfonatables 0. This fraction, therefore, was unchanged pentane. Fraction II was refractionated through the same column into narrower fractions. The results of this fractionation are given in Table 5.

TABLE 5

Results of Fractionation of the Fraction boiling at 40-95°

Fraction	Boiling range (°C)	Yield (% by volume)	n_D^{20}	d_4^{20}	Notes
I	33.4-42.4	6.1	1.3600	0.6301	8.4% of the losses in fractionation are added to the first two fractions
II	43 - 60.0	0.9	1.3802	0.6698	
III	60.4-73.0	10.8	1.4695	—	
IV	73.0-77.0		1.4722	—	
V	79.4-79.9	82.8	1.4998	—	
VI	Residue > 80°	17.2	—	—	

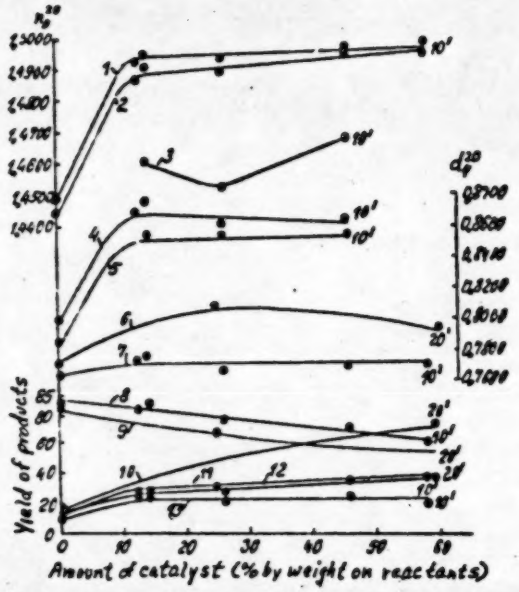


Fig. 4. Fractionation of the 95-200° fraction of the liquid product (see Table 7) of the destructive alkylation of benzene with pentane. Curves: 1) densities of fractions from secondary fractionation; 2) refractive indices of fractions from secondary fractionation; 3) secondary fractionation of the 95-200° fraction (section AB); 4) primary fractionation.

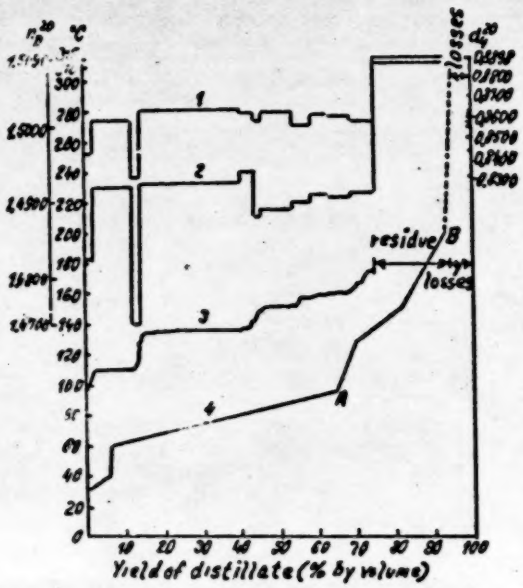


Fig. 3. Effect of amount of catalyst on yield of liquid reaction products: Expt. conditions: 460-470°, 420-520 atm, 10 and 20 minutes. Curves: 1) n_D^{20} fraction (150-200°); 2) n_D^{20} fraction (95-150°); 3) n_D^{20} "crude" product; 4) density, fraction (150-200°); 5) density, fraction (95-105°); 6) density, "crude" liquid product; 7) density, "crude" liquid product; 8) of whole liquid product; 9) of the whole liquid product; 10) of fraction boiling 95°, on liquid product; 11) of fraction boiling 95°, on reactants; 12) of fraction boiling 95°, on liquid product; 13) of fraction boiling 95°, on reactants

As the properties cited show, these fractions (64% of sulfonatables) consisted mainly of unchanged benzene, and they also contained products of the autodestructive alkylation of pentane. These fractions were not investigated in greater detail.

The fraction boiling at 95-200° was fractionated into three fractions with the properties set forth in Table 6.

In order to characterize the composition of this wide fraction in greater detail we carried out its precise rectification through a 50-plate column. Before rectification this fraction was treated at 0° with three portions (each 10% by volume) of 86% sulfuric acid. The product was was washed with caustic soda solution and with water, distilled over sodium, and dried over calcined calcium chloride; 97.5% of the original amount then remained. After this treatment the product had the following properties: n_D^{20} 1.4935, d_4^{20} 0.8639, amount of sulfonatables (by means

of Kattwinkel's mixture) 96%, and bromine number 0.84.

The results of the rectification of 250 ml of the fraction are given in Table 7 and represented graphically in Fig. 4.

TABLE 6

Fraction	Boiling range (°C)	Amount (%)	n_D^{20}	d_4^{20}	Molecular weight	Bromine number	Amount of sulfonatables (% by weight)
I	95-122	17.8	1.4894	0.8573	115	1.36	88.4
II	122-150	42.2	1.4909	0.8564	108	1.42	95.0
III	150-200	40.0	1.4948	0.8658	124	2.03	95.1

TABLE 7

Results of the Precise Rectification of the Fraction Boiling at 95-200°

Fraction	Boiling range	Yield (% by volume)		n_D^{20}	d_4^{20}	Molecular weight	Bromine number	Amount of sulfonatables (%)
		actual	cummulative					
I	95-109.0	1.8	1.8	1.4825	0.8431	–	–	–
II	109.5-111.0	10.2	12.0	1.4920	0.8597	94.0	–	96
III	111.3-128.0	2.0	14.0	1.4740	0.8313	–	–	–
IV	132.8-136.5	26.0	40.0	1.4925	0.8630	104	–	95.9
V	137.4-141.5	2.8	42.8	1.4941	0.8620	105	–	97.6
VI	140-148.5	2.6	45.4	1.4881	0.8578	109	–	88.6
VII	150.5-152.0	8.4	53.8	1.4890	0.8627	118	–	76.0
VIII	157 - 157.2	4.6	58.4	1.4900	0.8562	123	0.03	97.5
IX	158.5-159.8	4.4	62.8	1.4919	0.8614	122	0.0	97.6
X	160.3-162.0	5.8	68.6	1.4906	0.8605	117	0.0	82.0
XI	162.7-174.7	6.0	74.6	1.4912	0.8580	125	0.8	63.7
XII	>174.7	18.6	93.2	1.5082	0.8898	–	–	–
XIII	Losses	6.8	100.0	–	–	–	–	–

The residue in the flask (XII), amounting to 45 ml, was united with fractions boiling over the range 200-300° from all experiments, amounting to 72 ml, and the mixture was fractionated through a column. The results of this fractionation are given in Table 8.

TABLE 8

Results of Fractionation of Residues

Boiling range (°C)	Yield (% by volume)	n_D^{20}	d_4^{20}	Molecular weight
177-181	11.1	1.4945	0.8668	131
181-183	15.4	1.4952	0.8737	136
183-191	23.0	1.4996	0.8755	138
191-201	38.4	1.5042	0.8796	138
201-209	43.2	1.5250	0.9109	143
233-255	73.5	1.5862	0.9931	152
255-274	92.0	1.5884	0.9928	162
274-292	100.0	1.5840	0.9902	176

The residues from the fractionations were not investigated in greater detail. The densities, molecular weights, and refractive indices indicate the presence of aromatic hydrocarbons of high molecular weight.

For some of the narrow fractions obtained in the rectification (95-200° fraction), the molecular refractions were calculated. The values obtained are given in Table 9.

Certain fractions were investigated in Prof. M. M. Kusakov's labboratory by the Raman-spectra method. The measurements were carried out by M. Serebrennikova, to whom we express our thanks. The results obtained in this spectrum investigation are given in Table 10.

The fraction boiling over the range 150.5-152.8°, in which the presence of ethylmethylbenzenes could be presumed, was oxidized by the usual alkaline permanganate procedure. The acid so obtained did not melt below 300°, but sublimed. Elementary analysis of the acid gave the following results:

	%C	%H	%O
Found	57.62	3.80	38.6
	58.24	3.93	38.6
Calculated for phthalic acid	57.2	3.62	38.58

TABLE 9

Identification of the Narrow Fractions of the Product from their Molecular Refractions

Fraction	Boiling range	Supposed hydrocarbon	MR		Amount of sulfonatables	Purity of product (according to MR)
			Found	Calculated		
II	109.5-111.0	Toluene	31.8	30.925	96	97.5
IV	132.8-136.5	Ethylbenzene	35.1	35.543	95.9	98.7
V	137.4-141.5	Xylenes	35.6	36.643	97.6	97.5
VI	140 - 148.5	o-Xylene	37.9	36.643	88.6	96.5
VII	150.5-152.0	Isopropylbenzene	40.9	40.161	76.0	98.5
VIII	157 - 157.2	Propylbenzene	41.5	40.161	97.5	97.0
IX	158.5-159.8	1-Ethyl-3-methyl-benzene	41.5	40.161	97.6	97.0
X	160.3-162.0	1-Ethyl-4-methyl-benzene	39.4	40.161	82.0	98.0

TABLE 10

Results of the Spectrum Analysis of some of the Narrow Fractions

Fraction	Boiling range (°C)	n_D^{20}	d_4^{20}	Composition of fraction
IV	132.8-136.5	1.4925	0.8630	Consists mainly of ethylbenzene; traces of m-xylene were detected, and slight traces of ethylcyclohexane may be present
V	137.4-141.5	1.4941	0.8620	Consists of ethylbenzene and m xylene in the proportions of 3 : 1; some p-xylene and traces of o-xylene are present
VI	140 -148.5	1.4881	0.8378	Contains o-xylene with some m- and p-xylenes, and isopropylbenzene with some ethyl- and propyl-benzenes
VII	150 - 152	1.4890	1.8627	Contains isopropylbenzene with some propylbenzene

A sample of the acid (0.6458 g) was treated with 46 ml of methanol saturated with hydrogen chloride in a water bath for six hours. Water was then added, and a white mass of crystals came down. The yield of dry product after recrystallization from pentane was 0.4707 g. The crystals melted at 60°. The reported melting point of dimethyl isophthalate is 67-68°. Elementary analysis of dimethyl isophthalate:

	%C	%H	%O
Found	62.76	5.00	32.24
	62.68	5.20	32.12
Calculated for dimethyl phthalate	61.80	5.15	33.05

The results obtained by the oxidation of the investigated fraction confirm that it consisted essentially of ethylmethylbenzene.

The results that we have described prove fairly conclusively that the products of the reaction of pentane with benzene over an aluminosilicate catalyst under the given conditions are toluene, ethylbenzene, isomeric xylenes, isopropylbenzene, and other alkylated aromatic hydrocarbons.

Composition of the Gaseous Reaction Products

The gas formed in the interaction of benzene with pentane was fractionated in a low-temperature rectification apparatus (TsIATIM-51) and shown to contain the components listed in Table 11*.

* The analysis was carried out in the gas laboratory by Z. Nechaeva.

The analysis of the gas taken in conjunction with the results of the investigation of the liquid products enables us to form some views concerning the chemistry of the processes occurring in the course of the interaction of benzene with pentane.

TABLE 11

Analysis of the Gas

Component	Content (% by volume)	Notes
Hydrogen	8.2	The sp.gr. of the gas was about 1.0
Methane	33.0	
Ethane	40.5	
Propane	12.8	
Isobutane	2.0	
Residue	3.5	

We have previously shown [4] that in the thermal and thermocatalytic transformations of pentane in presence of an aluminosilicate catalyst the pentane undergoes destructive alkylation, which is preceded by the cracking of pentane, occurring, for example, according to the following equations:

$$C_5H_{12} \longrightarrow C_2H_4 + C_3H_8;$$

$$C_5H_{12} \longrightarrow C_4H_8 + CH_4;$$

$$C_5H_{12} \longrightarrow C_3H_6 + C_2H_6.$$

When benzene is present in the reaction mixture, the unsaturated hydrocarbons formed in this way may react with it with formation of the corresponding alkylbenzenes:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5;$$

$$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7 \text{ etc.}$$

Determinations of the free energy changes for some "overall" reactions of benzene and pentane show that they are all thermodynamically possible under the temperature conditions of our experiments. The presence of ethane, propane, and butane in the gaseous reaction products supports the view that the above reactions occur. The possibility is not excluded of the occurrence also of breakdown of pentane into free radicals, e.g. $C_5H_{12} \rightarrow C_3H_7 + C_2H_5$ or $C_5H_{12} \rightarrow C_5H_{11} + H$, and subsequent reaction of the free radicals with benzene.

It is noteworthy that in the reactions of pentane with benzene, but not in the earlier experiments on the autodestructive alkylation of pentane, the yield of the fraction boiling above 95° depends greatly on whether catalyst is present. This fact is probably associated with the directive influence of the aluminosilicate catalyst on the alkylation of benzene with the unsaturated hydrocarbons formed by the breakdown of the pentane. The primary act – the breakdown of the pentane – goes to approximately the same extent both in presence of aluminosilicate catalyst, and in its absence; but the secondary process – alkylation of benzene by unsaturated hydrocarbons – is accelerated by an aluminosilicate catalyst. The effects of other homogeneous and heterogeneous catalysts on the reaction of benzene with pentane are deserving of special study.

SUMMARY

1. The destructive alkylation of benzene with pentane over an aluminosilicate catalyst under autoclave conditions was effected for the first time.

2. The effects of the duration of reaction, temperature, and amount of catalyst on the yield of reaction products were investigated.

3. It was shown that destructive alkylation of benzene with an equimolecular amount of pentane under autoclave conditions results in the formation of a mixture of alkylated aromatic hydrocarbons (in an amount equal to 34% by weight of the original mixture) together with gaseous hydrocarbons (23% by weight on the original mixture).

4. The alkylated aromatic hydrocarbons obtained in the autoclave experiments were investigated, and it was shown that they included toluene, ethylbenzene, isopropylbenzene, xylenes, and ethylmethylbenzene. The gaseous reaction products were investigated and it was shown that they consisted mainly of saturated hydrocarbons.

LITERATURE CITED

[1] A. V. Grosse and V. N. Ipatyev, J. Gen. Chem 6, 1514 (1936).

[2] V. N. Ipatieff, V. Y. Komarewsky, H. Pines, J. Am. Chem. Soc. 58, 918 (1936).

[3] A. Sachanen, S. Davis, U. S. Patent 2234984.

[4] A. V. Topchiev, Ya. M. Paushkin, B. A. Krentsel, and I. M. Tolchinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 260 (See Consultant's Bureau Translation, p237.)

Received July 20, 1954

Petroleum Institute of the USSR Academy of Sciences

BLANK
PAGE

BEHAVIOR OF 3-, 4-, AND 5-ALKENYL HALIDES IN CONDENSATION REACTIONS WITH ALKYL HALIDES IN PRESENCE OF MAGNESIUM

M. A. Cheltsova, E. A. Chernyshev, and A. D. Petrov

It is known that the condensation reactions of allyl and 2-methylallyl halides with Grignard reagents derived from primary, secondary, and tertiary alkyl halides give high yields and so provide a convenient method for the synthesis of hydrocarbons. Whereas the presence of a double bond in the β-position with respect to halogen (2-alkenyl halides) results in greatly increased activity, as compared with the corresponding saturated alkyl halide, a double bond in the α-position (1-alkenyl halide) completely deactivates the halogen compound. We have recently shown that a double bond in the γ-position has a similar effect [1].

It was of great interest to determine whether this alternation of activity and inactivity continued further, i.e. in the 4- and 5-alkenyl halides. The present investigation was undertaken with the object of resolving this question, and in it we have confirmed the complete inactivity of 3-alkenyl halides, on the basis of new examples, and have shown that 4-alkenyl halides differ greatly from 2-alkenyl halides, their activities being only about 50% of those of the corresponding alkyl halides. Finally, it was found that a 5-alkenyl halide is active, but its activity is very little different from that of the corresponding alkyl halide. It was thus shown that the alternation of inactivity and enhanced activity in alkenyl halides is interrupted already when the double bond is in the δ-position (4-alkenyl halide), the activity then being not higher, as might be expected, but lower than that of the corresponding alkyl halide. In the 5-alkenyl halides, owing to the remoteness of the double bond with respect to the halogen the mutual effect of this bond and the halogen already approaches zero, and in activity this unsaturated halogen compound differs little from the corresponding saturated compound.

Condensation of Methylmagnesium Bromide with Tertiary 3-, 4-, and 5-Alkenyl Halides

We have shown previously that, whereas methylmagnesium bromide readily condenses with dimethylpropylmethyl chloride (2-chloro-2-methylpentane) with formation of 2,2-dimethylpentane, this reagent does not react with allyldimethylmethyl chloride (4-chloro-4-methyl-1-pentene) with formation of 4,4-dimethyl-1-pentene [1]. The inertness of 3-alkenyl halides was shown also by examples of the behavior of secondary and primary 3-alkenyl halides. In continuation of this work, in the present investigation we have shown that even when the double bond is tertiary, as in 4-bromo-2,4-dimethyl-1-pentene, the 3-alkenyl bromide does not condense with methylmagnesium bromide. The same is true of 4-bromo-4-phenyl-1-pentene.

4-Alkenyl halides were found to be quite different in reactivity. 5-Chloro-5-methyl-1-hexene condensed with methylmagnesium bromide with formation of 5,5-dimethyl-1-hexene in 10% yield. It is true that, in condensing with methylmagnesium bromide, 2-chloro-2-methylhexane formed 2,2-dimethylhexane in 20% yield, so that introduction of the δ-double bond reduced the yield, though not to zero as did the introduction of a γ-double bond in the tertiary alkyl halide of analogous structure. It is interesting that, contrary to expectation, the condensation of 5-bromo-5-methyl-1-hexene with $CH_2=CH-CH_2MgBr$ gave not a higher, but a lower yield than the corresponding reaction with CH_3MgBr. Ozonization of the resulting 4,4-dimethyl-1,7-octadiene showed that some 4,4-dimethyl-2,6-octadiene was present as impurity.

If double bonds can migrate into mutually closer positions during the condensation of alkenyl halides, then the possibility cannot be excluded of a partial migration of the double bond from the δ- to the γ-position in the original 5-bromo-5-methyl-1-hexene, and this could explain the relatively low yield of condensation products from 4-alkenyl halides and also the lower yield obtained from $CH_2=CH-CH_2MgBr$ than from CH_3MgBr. By the condensation of 6-bromo-6-methyl-1-heptene with methylmagnesium bromide a 13% yield of the previously undescribed 6,6-dimethyl-1-heptene was obtained. It is evident, therefore, that a double bond in the 5-position with respect to the halogen no longer has any effect on the activity.

Condensation of a Grignard Reagent derived from a Primary 3-Alkenyl Halide with Tertiary Alkyl Halides

We have shown previously [1] that 3-butenylmagnesium bromide does not react with tributylmethyl chloride

(5-butyl-5-chlorononane), whereas under the same conditions butylmagnesium bromide reacts with this chloro compound with formation of tetrabutylmethane (5,5-dibutylnonane) in 15% yield. In continuation of these experiments we have shown in the present investigation that a primary normal 4-alkenyl halide, unlike the analogous 3-alkenyl halide, will condense not only with 5-butyl-5-chlorononane, but also with tripropylmethyl chloride (4-chloro-4-propylheptane) and with trimethylmethyl chloride (2-chloro-2-methylpropane). Yields varied from 6 to 12%, i.e. were somewhat less than those of the C_{12}-C_{19} tetraalkylmethanes synthesized by us previously [2] by the condensation of 5-butyl-5-chlorononane and 4-chloro-4-propylheptane with primary alkyl halides under similar conditions in presence of mercuric chloride.

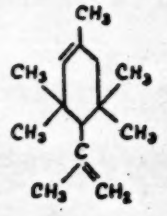
EXPERIMENTAL

1. Reaction of Allylmethylphenylmethyl Bromide (4-Bromo-4-phenyl-1-pentene) with CH_3MgBr. The reaction, like that of this reagent with 4-halo-4-methyl-1-pentenes, did not go. The only substance isolated was the product of the hydrolysis of the original bromo compound, allylmethylphenylmethanol (2-phenyl-4-penten-2-ol).

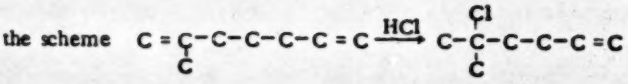
2. Reaction of 4-Bromo-2,3-dimethyl-1-pentene with CH_3MgBr. 2,4-Dimethyl-4-penten-2-ol was prepared from 2-methylallyl chloride and acetone by Yarovsky's method in 46% yield. Altogether 300 g of the alcohol was prepared, and this by treatment with phosphorus tribromide gave a 23.5% yield of 4-bromo-2,4-dimethyl-1-pentene; b.p. 50-52° (30 mm); n_D^{20} 1.4645; d_4^{20} 1.1450; Found MR 42.73; Calculated MR 41.83. When this bromo compound (86 g) was added to excess of methylmagnesium bromide there was a rise in temperature. When the addition was complete, the mixture was heated in a water bath. The greater part of the ether was distilled off, and the mixture was again heated at 60-70° for ten hours. Fractional distillation yielded the following three fractions:

Frac. I,	b.p. 80-83°;	n_D^{20} 1.4170 ;	10 g
Frac. II,	b.p. 97-100°;	n_D^{20} 1.4220; d_4^{20} 0.7287;	3 g
Frac. III,	b.p. 213-215°;	n_D^{20} 1.4785;	16.5 g; yield 33.5%

Fractions I and II were identified as mixtures of 2,4-dimethyl-1,3-pentadiene and 2,4-dimethyl-1,4-pentadiene, and they contained traces of a 2,4,4-trimethylpentene (probably 2,4,4-trimethyl-2-pentene) as indicated by the Raman spectrum (the frequency 756 cm^{-1}). Fraction III consisted of the cyclic dimer of 2,4-dimethylpentadiene. The presence of a tertiary carbon atom and of two double bonds was indicated by the frequencies: 373, 343, 575, 766, 905, 927, 935, 1125, 1150, 1266, 1304, 1356, 1377, 1427, 1628, 1641, 1677, 2998 cm^{-1}. In the ozonization products formic acid and a nonvolatile acid, giving a silver salt containing 31.16% Ag, were detected. It is probable that the hydrocarbon was identical with the cyclic dimer of 2,4-dimethyl-1,3-pentadiene prepared by Merezhkovsky [1]. Oxidation of this hydrocarbon should yield a diketo acid giving a silver salt containing 30.95% Ag.



3. Reaction of 5-Chloro-5-methyl-1-hexene with CH_3MgBr and of 5-Bromo-5-methyl-1-hexene with $CH_2 = CH - CH_2MgBr$. 5-Chloro-5-methyl-1-hexene was synthesized from 2-methyl-1,5-hexadiene, which was prepared by Yarovsky's method by addition of a mixture of 2-methylallyl chloride and allyl bromide to magnesium. 2-Methyl-1,5-hexadiene had b.p. 86-88°; d_4^{20} 0.7257; n_D^{20} 1.4180; Found MR 33.7; Calculated MR 33.59; it was obtained in 30% yield.

Addition of HCl according to the scheme 

gave a 50% yield of 5-chloro-5-methyl-1-hexene, b.p. 131-132° (748 mm); n_D^{20} 1.4330; d_4^{20} 0.8842; Found MR 38.95; Calculated MR 38.93; Found 26.99% Cl; Calculated for $C_7H_{13}Cl$ 26.79% Cl; Calculated M 132.5; Calculated M 130.5.

By condensation of 132 g of 5-chloro-5-methyl-1-hexene with methylmagnesium bromide 11 g (10%) of 5,5-dimethyl-1-hexene was obtained; it had b.p. 100-102°; n_D^{20} 1.4030; d_4^{20} 0.7136; Found MR 38.80; Calculated MR 38.68.

The synthesis of 5-bromo-5-methyl-1-hexene was carried out by the same route; it had b.p. 87-89° (95 mm); d_4^{20} 1.1664; n_D^{20} 1.4605; Found MR 41.59; Calculated for $C_7H_{13}Br$ MR 41.82.

	Found %:	C 47.57; H 7.60; Br 45.08
$C_7H_{13}Br$.	Calculated %:	C 47.45; H 7.41; B4 45.14

The bromo compound (330 g) was added to allylmagnesium bromide prepared from 400 g of allyl bromide. The mixture was heated in a water bath for 20 hours, and then, after removal of ether, it was heated at 80-90° for ten hours. The product was 12.4 g of 4,4-dimethyl-1,7-octadiene, formed as follows:

$$CH_2=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br + CH_2=CH-CH_2MgBr \longrightarrow$$

$$\longrightarrow CH_2=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH=CH_2$$

The yield was thus only 5%. The substance had b.p. 145-148°; d_4^{20} 0.7647; n_D^{20} 1.4330; Found M 138.4; calculated M 138.1

	Found %:	C 86.0; H 13.88
$C_{10}H_{18}$.	Calculated %:	C 86.55; H 13.05

The 4,4-dimethyl-1,7-octadiene was hydrogenated to 4,4-dimethyloctane, b.p. 152-154°; n_D^{20} 1.4132; d_4^{20} 0.7225; Found MR 49.09; calculated MR 49.38. The frequencies 756, 913, 931, 1196, and 1231 cm^{-1} in the Raman spectrum confirmed the presence of a quaternary carbon in the middle of the chain of this hydrocarbon.

4,4-Dimethyl-1,7-octadiene was ozonized. The products identified were formic acid (calomel), acetic acid (silver salt containing 64.64% Ag), and dimethylsuccinic acid, m.p. 137°; found M 153.2; calculated M 146; found 59.92% Ag; calculated 59.96% Ag. 3,3-Dimethylhexanedioic acid was also identified; found 55.17% Ag, calculated 55.50% Ag.

The frequencies 769, 912, 937, 1196, 1235 and 750, 910, 930, 1200, 1250 cm^{-1} in the Raman spectrum confirmed the presence of a quaternary carbon atom and of two double bonds at the extreme ends of the chain, but there was also a small amount of a hydrocarbon having double bonds in the two penultimate positions. It follows, therefore, both from the oxidation results and from the spectra, that the 4,4-dimethyl-1,7-octadiene was associated with some 4,4-dimethyl-2,6-octadiene. The lowness of the yield of the required diene prompted us to identify the remaining products: it was found that there was 50% of unchanged bromo compound (5-bromo-5-methyl-1-hexene) and 30% of the diolefin resulting from its dehydrohalogenation.

4. Reaction of 6-Bromo-6-methyl-1-heptene with CH_3MgBr. The starting material for the preparation of 6-bromo-6-methyl-1-heptene was 2-furaldehyde, which was hydrogenated at 150° under an initial pressure of 100 atm: 2600 g of 2-furaldehyde yielded 1900 g of tetrahydrofurfuryl alcohol, b.p. 170-175°. From this alcohol 520 g of tetrahydrofurfuryl bromide was prepared by the action of phosphorus tribromide. Tetrahydrofurfuryl bromide was converted into 4-penten-1-ol, from which 572 g of 5-bromo-1-pentene, b.p. 125-126°, was obtained. From 5-bromo-1-pentene, as its Grignard reagent, and acetone 2-methyl-6-hepten-2-ol was prepared as follows. The Grignard reagent was prepared from 149 g (1 mole) of 5-bromo-1-pentene and 24 g of magnesium, and 45 g (0.8 mole) of acetone was added at 0°. The mixture was heated in a water bath, cooled, and decomposed with 10% acetic acid. The experiment was repeated several times, and 572 g of 5-bromo-1-pentene gave 304 g of 2-methyl-6-hepten-2-ol, b.p. 162° (756 mm); n_D^{20} 1.4380; d_4^{20} 0.8423; found MR 39.93; calculated for $C_8H_{16}O$ MR 40.20; found (by Tserevitinov's method) OH 12.20%; calculated OH 13.20%.

6-Bromo-6-methyl-1-heptene was prepared as follows. A mixture of 154 g of 2-methyl-6-hepten-2-ol and 20 g of dry pyridine was added gradually at − 5° to 110 g of freshly distilled phosphorus tribromide. From the resulting mixture, 115 g of a bromo compound boiling at 65-66° (20 mm) was isolated. The experiment was

repeated, and altogether 230 g of the bromo compound was obtained; it had d_4^{20} 1.1163; n_D^{20} 1.4640; found MR 47.24; for $C_8H_{15}Br$ calculated MR 46.23. When 114 g (0.6 mole) of 6-bromo-6-methyl-1-heptene was added to methylmagnesium bromide prepared from 36 g (1.5 moles) of magnesium, no rise in temperature was observed. When the whole of the bromo compound had been added, the reaction mixture was heated for ten hours, after which the greater part of the ether was removed and the mixture was again heated for ten hours at 60-70°. The experiment was repeated. Fractionation through an 18-plate column yielded 20 g (10%) of a product having b.p. 128-130°; n_D^{20} 1.4220; d_4^{20} 0.7465; found MR 42.94; calculated for C_9H_{18} MR 43.30; iodine number found 205; calculated 202; found: 85.80% C; 14.22% H; calculated for C_9H_{18} 85.62% C; 14.38% H.

The presence of the frequencies 1645, 2998, and 1296 cm^{-1} in the Raman spectrum indicated that the hydrocarbon contained a tertiary carbon atom and a double bond, mainly terminal, but to some extent also in the penultimate position. Ozonization yielded formic acid and an acid of m.p. 34° and molecular weight 144.5. Analysis of the silver salt gave 43.35% Ag. Dimethylhexanoic acid $C_8H_{16}O_2$ has a molecular weight of 144.23 and its silver salt contains 42.96% Ag. The hydrocarbon obtained, therefore, was the previously undescribed 6,6-dimethyl-1-heptene in admixture with about 5% of 6,6-dimethyl-2-heptene, the presence of which was established only by the optical method (among the ozonization products we were unable to detect either acetic acid or dimethylvaleric acid).

6,6-Dimethyl-1-heptene was hydrogenated to give 2,2-dimethylheptane, b.p. 128°, n_D^{20} 1.4030; d_4^{20} 0.7157, these constants being close to those given in the literature for 2,2-dimethylheptane (b.p. 130.4°; n_D^{20} 1.4024; d_4^{20} 0.7105).

5. Reaction of 4-Pentenylmagnesium Bromide with 5-Butyl-5-chlorononane. A Grignard reagent was prepared from 80 g (0.54 mole) of 4-pentenyl bromide and 12.8 g of magnesium in 150 ml of absolute ether, 5 g of mercuric chloride was added, and then 100 g (0.46 mole) of 5-butyl-5-chlorononane was added dropwise at 15-25° over a period of five hours. After the whole of the chlorocompound had been added, stirring was continued for three hours, and the mixture was then heated at the boiling point of ether for a further three hours. A voluminous white precipitate was formed. The mixture was stirred at room temperature for about 20 hours and was then decomposed with water and 10% hydrochloric acid. The ether layer was washed with weak sodium carbonate solution and with water, united with the ether extract, and dried over calcium chloride. The ether was distilled off, and the residue was vacuum-fractionated. The fractionation yielded 67.6 g of the dehydrochlorination product 5-butyl-4-nonene, b.p. 90-93° (10 mm) and n_D^{20} 1.4369; 3.8 g of a fraction boiling at 93-139° (10 mm), and 6.9 g of 6,6-dibutyl-1-decene, b.p. 139-141° (10 mm); n_D^{20} 1.4480; d_4^{20} 0.7987; found MR 84.83; calculated MR 85.00; yield 6.1%.

	Found %:	C 85.75; 85.82; H 14.28; 14.34
$C_{18}H_{36}$.	Calculated %:	C 85.62; H 14.38

6. Reaction of 4-Pentenylmagnesium Bromide with 4-Chloro-4-propylheptane. The reactants were 74.5 g (0.5 mole) of 4-pentenyl bromide, 12 g (0.5 mole) of magnesium, and 70.5 g (0.4 mole) of 4-chloro-4-propylheptane. The procedure and conditions were as in the previous experiment. After the necessary treatment the ether was distilled off and the residue was vacuum-fractionated. The fractionation yielded 43.6 g of the dehydrochlorination product 4-propyl-3-heptene, b.p. 62-65° (20 mm) and n_D^{20} 1.4348, 2.3 g of a fraction boiling at 64-123° (20 mm), and 7.1 g (8.4%) of 6,6-dipropyl-1-nonene, b.p. 123-125° (20 mm); n_D^{20} 1.4408; d_4^{20} 0.7825; calculated MR 71.11; found MR 70.98.

	Found %:	C 85.52; 85.74; H 14.28; 14.30
$C_{15}H_{30}$.	Calculated %:	C 85.62; H 14.38

7. Reaction of 4-Pentenylmagnesium Bromide with tert-Butyl Chloride. The reaction was carried out by the same procedure and under the same conditions as the reaction described in Section 5. During the reaction isobutene gas was evolved. The substances taken for reaction were 149 g (1 mole) of 4-pentenyl bromide, 24 g of magnesium, and 73.5 g (0.8 mole) of tert-butyl chloride. Fractionation through an 18-plate column yielded 8.6 g of 2,4,4-trimethyl-2-pentene, b.p. 101-105.5°, n_D^{20} 1.4108; d_4^{20} 0.7186, and 11.7 g (11.7%) of 6,6-dimethyl-1-heptene, b.p. 125.5-126.5° (758 mm); n_D^{20} 1.4212; d_4^{20} 0.7395; calculated MR 43.33; found MR 43.16.

	Found %:	C 85.72; 85.78; H 14.30; 14.28
C_9H_{18}.	Calculated %:	C 85.63; H 14.37

We express our deep gratitude to M. I. Batuev, who carried out the spectrum analysis of the hydrocarbons that we prepared.

SUMMARY

1. In a study of the reactions of methylmagnesium bromide with 4-bromo-4-phenyl-1-pentene and with 4-bromo-2,4-dimethyl-1-pentene we have obtained further confirmation of the inactivity in condensation reactions of alkenyl halides having a γ-double bond.

2. In a study of the condensations of 5-chloro-5-methyl-1-hexene with methylmagnesium bromide, of 5-bromo-5-methyl-1-hexene with allylmagnesium bromide, and of 4-pentenylmagnesium bromide with 5-butyl-5-chlorononane, with 4-chloro-4-propylheptane, and with 2-chloro-2-methylpropane, we have shown that alkenyl halides having a δ-double bond, both tertiary and primary, condense with formation of olefins in a yield that is only about 50% of that obtained in the corresponding reactions with the corresponding alkyl halides.

3. Taking the condensation of 6-bromo-6-methyl-1-heptene with methylmagnesium bromide as example, we have shown that a double bond in the ε-position with respect to the halogen has no longer any effect on the activity of the halogen compound, which reacts with Grignard reagents and gives the same yields as the corresponding alkyl halides. It has thus been shown that the alternation of inactivity (α- and γ-double bonds) with activity (very high for a β-double bond and low when the double bond is in the δ-position) is interrupted when the double bond reaches the δ-position.

4. The following substances were synthesized for the first time: 2-methyl-6-hepten-2-ol, 6-bromo-6-methyl-1-heptene, 6,6-dimethyl-1-heptene (by two methods), 6,6-dipropyl-1-nonene, and 6,6-dibutyl-1-decene. Raman spectra have been determined for some of the compounds prepared.

Received May 8, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] A. D. Petrov, M. A. Cheltsova, and E. A. Chernyshev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 6, 1087.•

[2] A. D. Petrov and E. A. Chernyshev, Proc. Acad. Sci. USSR 86, No. 5, 957 (1952).

• Consultant's Bureau Translation, p 949.

BLANK
PAGE

SYNTHESIS OF ORGANOSILICON ESTERS OF PROPIONIC AND ISOBUTYRIC ACIDS, AND THEIR PROPERTIES

D. N. Andreev, B. N. Dolgov, and E. V. Kukharskaya

Organosilicon esters derived from alkylsilanes have not yet received adequate study. The compounds described in the literature are mainly acetoxysilanes in which silicon is attached to alkyl [1-4], alkenyl [5], chloroalkyl [6], or aryl [7] radicals. Very few organosilicon esters of monobasic acids higher than acetic are known [8, 9]. In particular, practically no derivatives of propionic and isobutyric acids have been described. Only four such compounds are known: tetrakis(propionyloxy)silane [10], tetrakis(butyryloxy)silane [11], and ethyltris- and diethylbis-(propionyloxy) silanes, which were described in a patent [12].

We now describe the synthesis and properties of twelve organosilicon esters of propionic and isobutyric acids, of which ten have been prepared for the first time. They are derivatives of methyl- and ethyl-silanes in which various numbers of alkyl and acyloxy groups are attached to silicon. They were prepared by the reaction of alkylchlorosilanes with sodium salts of the acids [2] according to the equation:

$$R_{4-x}SiCl_x + x\,NaOOCR' \longrightarrow R_{4-x}Si(OOCR')_x + x\,NaCl.$$

The esters so obtained are clear colorless liquids that are readily hydrolyzed by water. As the number of acyloxy groups attached to silicon increases, the rate of hydrolysis also increases. One result of this was that we were unable to determine the molecular weights of alkyltris(acyloxy)silanes. The densities of the synthesized esters increase in regular manner as the methyl or ethyl radicals are replaced by acyloxy groups. The refractive index varies as follows: replacement of methyl by acyloxy results in a regular rise in refractive index, but replacement of ethyl by the same acyloxy groups results in a slight fall in refractive index.

TABLE 1

No.	Ester	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	M found	M calculated	MR found	MR calculated	Yield (%)
I	Trimethyl(propionyloxy)silane	$(CH_3)_3SiOOCC_2H_5$	122-123 (757)	0.8614	1.3931	147	146.23	40.51	40.30	41.1
II	Dimethylbis(propionyloxy)silane	$(CH_3)_2Si(OOCC_2H_5)_2$	83.5-84 (10)	1.0057	1.4086	197	204.26	50.17	50.32	61.7
III	Methyltris(propionyloxy)silane	$CH_3Si(OOCC_2H_5)_3$	139 (15)	1.0939	1.4140	–	262.30	59.91	50.34	50.9
IV	Triethyl(propionyloxy)silane	$(C_2H_5)SiOOCC_2H_5$	83-85 (14)	0.8885	1.4202	183	188.31	53.66	54.19	63.8
V	Diethylbis(propionyloxy) silane	$(C_2H_5)_2Si(OOCC_2H_5)_2$	108.5-109.5(13)	0.9896	1.4193	232	232.32	59.32	59.58	45.9
VI	Ethyltris(propionyloxy)silane	$C_2H_5Si(OOCC_2H_5)_3$	119 (5)	1.0660	1.4180	–	276.33	64.22	64.97	51.5
VII	(Isobutyryloxy)-trimethylsilane	$(CH_3)_3SiOOCCH(CH_3)_2$	43.5-44 (20)	0.8501	1.3950	166	160.26	45.10	44.93	47.3
VIII	Bis(isobutyryloxy)-dimethylsilane	$(CH_3)_2Si[OOCCH(CH_3)_2]_2$	95-95.5 (13)	0.9751	1.4057	234	232.32	59.35	59.58	72.9
IX	Tris(isobutyryloxy)-methylsilane	$CH_3Si[OOCCH(CH_3)_2]_3$	126-127 (12)	1.0223	1.4090	–	304.38	73.97	74.23	26.3
X	Triethyl(isobutyryloxy)silane	$(C_2H_5)_3SiOOCCH(CH_3)_2$	88 (14)	0.8743	1.4190	200	202.34	58.59	58.82	65.3
XI	Diethylbis(isobutyryloxy)silane	$(C_2H_5)_2Si[OOCCH(CH_3)_2]_2$	123-125 (19)	0.9538	1.4160	268	260.37	68.77	68.84	53.2
XII	Ethyltris(isobutyryloxy)silane	$C_2H_5Si[OOCCH(CH_3)_2]_3$	129 (5)	1.0144	1.4140	–	318.41	78.81	78.86	35.9

EXPERIMENTAL

For all of the syntheses the procedure was as follows. The sodium salt of the acid (0.1-0.5 mole), which had been dried at 100-110° for four hours, was introduced into a round-bottomed flask fitted with reflux condenser, which was connected to a system of air driers, a mercury-sealed mechanical stirrer, and a dropping funnel. Dry petroleum ether (100-500 ml, freshly distilled over sodium) was added, and the mixture was stirred while a solution of one part of the alkylchlorosilane in one part of dry petroleum ether was added from the dropping funnel. Reaction occurred with evolution of heat. When the whole of the alkylchlorosilane had been added, the mixture was stirred at the boiling point of petroleum ether for 8-12 hours. When the mixture was cool, the liquid part was separated from the precipitate of salts by filtration through a sintered glass filter in an atmosphere of dry air. Petroleum ether was distilled off, and the reaction products were fractionated twice under reduced pressure in a current of dry air.

Constants of the synthesized esters are given in Table 1, and analytical data in Table 2. The yields given for the esters refer to the narrow fractions obtained after the second fractionation, which are described in the table. The molecular weights of the esters were determined cryoscopically in benzene, ester numbers were determined by hydrolysis of a weighed sample of the substance with a solution of caustic potash in ethylene glycol [13], and molecular refractions were calculated from Warrick's component values [14]. Silicon was determined in a weighed amount of ester by mineralization with a mixture of concentrated sulfuric and nitric acids. We did not succeed in determining silicon in (I), (II), (VII), and (VIII) by this method; for these we give the results of analysis for carbon and hydrogen.

TABLE 2

No.	Ester number		Amount Si (%)		Amount of C (%)		Amount of H (%)	
	found	calculated	found	calculated	found	calculated	found	calculated
I	379	383	–	–	46.69	49.27	9.89	9.65
II	541	549.3	–	–	47.14	47.03	7.88	7.89
III	650	642	10.72	10.69	–	–	–	–
IV	302	297	14.42	14.90	–	–	–	–
V	488	482	11.87	12.08	–	–	–	–
VI	618	609	9.93	10.15	–	–	–	–
VII	350	350	–	–	52.13	52.45	9.74	10.06
VIII	485	483	–	–	51.49	51.68	8.71	8.67
IX	577	552	9.32	9.22	–	–	–	–
X	277	277	13.48	13.86	–	–	–	–
XI	423	428	10.34	10.78	–	–	–	–
XII	528	526	8.37	8.81	–	–	–	–

SUMMARY

Twelve organosilicon esters, of which ten are here described for the first time, were synthesized by the action of methyl- and ethyl-chlorosilanes on the sodium salts of propionic and isobutyric acids.

LITERATURE CITED

[1] R. O. Sauer, W. J. Patnode, J. Am. Chem. Soc. 67, 1548 (1945).

[2] H. A. Schuyten, J. W. Weaver, J. D. Reid, J. Am. Chem. Soc. 69, 2110 (1947).

[3] R. O. Sauer, J. Am. Chem. Soc. 68, 138 (1946).

[4] K. A. Andrianov, A. A. Zhdanov, and A. A. Bogdanova, Proc. Acad. Sci. USSR 94, 697 (1954).

[5] K. C. Frisch, P. A. Goodwin, R. E. Scott, J. Am. Chem. Soc. 74, 4584 (1952).

[6] F. C. Boye, H. W. Post, J. Org. Chem. 17, 1386 (1952).

[7] N. S. Nametkin, A. V. Topchiev, and F. F. Machus, Proc. Acad. Sci. USSR 87, 233 (1952).

[8] D. N. Andreev and L. L. Shchukovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 1, 135.*

* Consultant's Bureau Translation, p 121

[9] B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, J. Gen. Chem. 24, No. 9, (1954).

[10] F. G. Launing, J. Am. Chem. Soc. 75, 1596 (1953).

[11] K. D. Petrov and M. I. Itkina, J. Gen. Chem. 17, 220 (1947).

[12] C. A. MacKenzie, M. Schoffman, U. S. Pat. 2537073 (9/1 1951); C. A. 45, 3410 (1951).

[13] L. N. Petrova and O. V. Shvarts, Analysis of Synthetic Perfumes, 1941, p. 65, Food Indust. Press.

[14] E. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

Received May 19, 1954

Institute of Silicate Chemistry of the USSR Academy of Sciences

BLANK
PAGE

REACTIONS OF EPICHLOROHYDRIN AND OF GLYCIDOL WITH ORGANOCHLOROSILANES

K. A. Andrianov, N. N. Sokolov, E. N. Khrustaleva, and L. N. Yukina

The reactions of α-epoxides with organohalosilanes have received little study. There are only two papers relating to the reactions of ethylene oxide with organochloro- and organobromo-silanes. In one of these [1] the products are described of the reaction of some organochlorosilanes with ethylene oxide according to the equation:

$$R_nSiCl_{4-n} + (4-n)\,CH_2\!-\!CH_2 \rightarrow R_nSi(OCH_2CH_2Cl)_{4-n}.$$

In the second paper [2] the reactions of tribromomethylsilane and dibromodimethylsilane with ethylene oxide are described. Reactions of epoxides with organohalosilanes are, however, of interest in that they enable Si – O – C links to be obtained without the elimination of hydrogen halide. This peculiar feature of these reactions is applied, for example, in the preparation of certain organic polysiloxanes [3] and in the resolution of azeotropes of organosilicon compounds [4].

We have studied the reactions of epichlorohydrin and of glycidol with organochlorosilanes, and have found that they proceed according to the equations:

$$R_nSiCl_{4-n} + (4-n)\,CH_2\!-\!CHCH_2Cl \rightarrow R_nSi(OCH_2\underset{Cl}{CH}CH_2Cl)_{4-n}. \qquad (1)$$

$$R_nSiCl_{4-n} + (4-n)\,CH_2\!-\!CHCH_2OH \rightarrow R_nSi(OCH_2\underset{Cl}{CH}CH_2OH)_{4-n}. \qquad (2)$$

As a result of reactions proceeding according to Equation 1, we have prepared the compounds that are listed with their formulas and some of their properties in Table 1. Some compounds prepared according to Equation 2 are listed in Table 2. All of these reactions were exothermic, and the heat evolved was particularly great in the reactions with terfunctional organochlorosilanes. Also, it was found that the reactivity of the α-epoxy ring was so great that reaction of the hydroxyl of glycidol with the chlorine of the organochlorosilane either did not go, or went to only a slight extent. The compounds obtained readily underwent hydrolysis, especially in presence of hydrochloric acid.

It is known that reactions with unsymmetrical α-epoxides can proceed in two directions. Thus, isobutylene oxide (1,2-epoxy-2-methylpropane), treated with HCl, gives two parts of 1-chloro-2-methyl-2-propanol and one part of 2-chloro-2-methyl-1-propanol. Hence, in order to determine the structures of the compounds obtained in accordance with Equations 1 and 2, the product of the reaction of chlorotrimethylsilane and epichlorohydrin was submitted to hydrolysis.

$$(CH_3)_3SiCl + CH_2\!-\!CHCH_2Cl \rightarrow \begin{cases} (CH_3)_3SiOCH_2CHClCH_2Cl & (a) \\ ClCH_2\!-\!\underset{OSi(CH_3)_3}{CH}\cdot CH_2Cl & (b) \end{cases} \qquad (3)$$

We showed that hydrolysis of the compounds formed according to Equation 3 yields the corresponding alkylsilanols and dichloropropanols. In the given case, hydrolysis of the product formed in accord with Equation 3 (a) would yield trimethylsilanol and 2,3-dichloro-1-propanol:

$$(CH_3)_3SiOCH_2CHClCH_2Cl + H_2O \rightarrow (CH_3)_3SiOH + HOCH_2CHCl\,CH_2Cl$$

The product formed by Equation 3 (b) would give trimethylsilanol and 1,3-dichloro-2-propanol:

$$ClCH_2\!-\!\underset{OSi(CH_3)_3}{CH}\!-\!CH_2Cl + H_2O \rightarrow (CH_3)_3SiOH + ClCH_2CHOHCH_2Cl.$$

TABLE 1

Substance (°C)	Formula	B.p. in °C (p in mm)	Freezing point	d_4^{20}	n_D^{20}	MR found	MR calculated
Tris(2,3-dichloropropoxy)methylsilane	$CH_3Si(OCH_2-CH(Cl)-CH_2Cl)_3$	–	−83–85	1.3452	1.4906	88.50	89.51
Bis(2,3-dichloropropoxy)dimethylsilane	$(CH_3)_2Si(OCH_2-CH(Cl)-CH_2Cl)_2$	160–165 (37)	−93–97	1.2720	1.4772	64.80	69.70
(2,3-Dichloropropoxy)trimethylsilane	$(CH_3)_3Si(OCH_2-CH(Cl)-CH_2Cl)$	96–100 (66)	−55–57	1.1094	1.4456	45.4	49.0
Bis(2,3-dichloropropoxy)methylsilane	$CH_3SiH(OCH_2-CH(Cl)-CH_2Cl)_2$	173-175 (34)	−55–57	1.3740	1.4782	58.8	65.3
Tris(2,3-dichloropropoxy)ethylsilane	$C_2H_5Si(OCH_2-CH(Cl)-CH_2Cl)_3$	–	−47	1.3740	1.4880	91.2	94.0
Bis(2,3-dichloropropoxy)diethylsilane	$(C_2H_5)_2Si(OCH_2-CHCH_2Cl)_2$ (Cl)	150–200 (36)	−89	–	1.4815	–	–
(2,3-Dichloropropoxy)triethylsilane	$(C_2H_5)_3Si(OCH_2-CH(Cl)-CH_2Cl)$	65–70 (100)	−68	1.0776	1.4492	61.7	63.0
Bis(2,3-dichloropropoxy)ethylsilane	$C_2H_5SiH(OCH_2CH(Cl)-CH_2Cl)_2$	185–190 (34)	−60–65	1.2992	1.4790	65.7	70.44
Tris(2,3-dichloropropoxy)phenylsilane	$C_6H_5Si(OCH_2CH(Cl)-CH_2Cl)_3$	–	−68	1.3666	1.5247	106.10	107.61
Tetrakis(2,3-dichloropropoxy)silane	$Si(OCH_2CH(Cl)-CH_2Cl)_4$	–	−76	1.4590	1.5017	106.9	109.0

It is known that epichlorohydrin cannot be obtained from 2,3-dichloro-1-propanol by the action of alkalis; only 1,3-dichloro-2-propanol will give it under such conditions. Experiments in which the product of the reaction of Equation 3 was hydrolyzed and attempts were made to obtain epichlorohydrin from the dichloropropanol formed gave negative results, as against positive results obtained with pure 1,3-dichloro-2-propanol. Equations 1 and 2, therefore, represent the actual course of the process and the structures of the compounds obtained.

Epichlorohydrin and glycidol were treated not only with organochlorosilanes, but also with silicon tetrachloride. In the course of the work various methods for the preparation of epichlorohydrin and glycidol were examined and improved. It should be noted that the products of the reaction of organochlorosilanes with glycidol, alkyl(2-chloro-3-hydroxypropoxy)silanes, are unstable to hydrolysis and to heat, and we were unable to rectify many of them without decomposition, great difficulties were met in the analysis of these compounds.

TABLE 2

Substance	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	OH content (%) found	OH content (%) calculated	Cl content (%) found	Cl content (%) calculated
(2-Chloro-3-hydroxypropoxy)-trimethylsilane	$(CH_3)_3SiOCH_2CHClCH_2OH$	82-84 (18)	1.1331	1.4443	8.9	9.31	19.4	19.41
Bis(2-chloro-2-hydroxypropoxy)dimethylsilane	$(CH_3)_2Si(OCH_2CHClCH_2OH)_2$	108 (20)	1.2267	1.4720	11.7	12.27	25.6	25.57
Tris(2-chloro-3-hydroxypropoxy)methylsilane	$CH_3Si(OCH_2CHClCH_2OH)_3$	97 (16)	1.3219	1.4837	13.8	13.72	28.7	28.6

EXPERIMENTAL

1. Preparation of Epichlorohydrin

We obtained epichlorohydrin by the reaction of 1,3-dichloro-2-propanol with calcium hydroxide [6]. The 1,3-dichloro-2-propanol was prepared by saturating glycerol with hydrogen chloride [7]. It was found that the hydrolysis of silcon tetrachloride formed a very convenient method of preparing a continuous flow of hydrogen chloride for this purpose:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl.$$

The hydrogen chloride was prepared in a reactor fitted with reflux condenser, thermometer, dropping funnel, and hermetically sealed stirrer. Water was introduced into the reactor and heated to 70-80°, and a mixture (1 : 1 by weight) of silicon tetrachloride and toluene was added gradually from the dropping funnel, the end of which was below the level of the water (toluene acted as a diluent). After passing through a drying system, the hydrogen chloride was passed to the vessel containing glycerol.

A 68% yield of 1,3-dichloro-2-propanol was obtained. It boiled at 72-76° (14 mm), its density was 1.359 ± 0.005, and its chlorine content was 53-55% (calculated 54.9%). The epichlorohydrin used in our experiments boiled at 115-118°. It had a chlorine content of 37.0-38.0% (calculated 37.8%) and an epoxy content of 44.0-46.6% (calculated 46.7%).

2. Preparation of Glycidol

Glycidol was prepared by the action of caustic soda on 3-chloro-1,2-propanediol [8]. It was obtained in 55-60% yield. It boiled at 61-63° (12 mm), and it had an epoxy content of 54% (calculated 58.01%). The characteristics of the organochlorosilanes and of the silicon tetrachloride used in the syntheses are given in Table 3.

TABLE 3

Silicon compound	Formula	B.p. (°C)	Chlorine content (%)
Trichloromethylsilane. . . .	CH_3SiCl_3	67	71.4
Dichlorodimethylsilane. . .	$(CH_3)_2SiCl_2$	69.5	55.1
Chlorotrimethylsilane. . . .	$(CH_3)_3SiCl$	57	32.7
Dichloromethylsilane. . . .	CH_3SiHCl_2	41	61.6
Trichloroethylsilane.	$C_2H_5SiCl_3$	97.5	65.4
Dichlorodiethylsilane. . . .	$(C_2H_5)_2SiCl_2$	129	45.2
Chlorotriethylsilane.	$(C_2H_5)_3SiCl$	143	23.4
Dichloroethylsilane.	$C_2H_5SiHCl_2$	74.5	54.8
Trichlorophenylsilane. . . .	$C_6H_5SiCl_3$	201	50.3
Silicon tetrachloride.	$SiCl_4$	56	83.4

3. Reactions of Epichlorohydrin with Organochlorosilanes

Tris(2,3-dichloropropoxy)methylsilane. Epichlorohydrin (27.7 g, i.e. 0.3 mole) was placed in a flask fitted with reflux condenser, dropping funnel, thermometer, and hermetically sealed stirrer, and it was stirred while 14.9 g (0.1 mole) of trichloromethylsilane was added over a period of two hours. Reaction set in after the first few drops of trichloromethylsilane had been added, and the evolution of heat was only slight. The temperature in the flask was maintained within the range 27-35° by controlling the rate of addition of the trichloromethylsilane. When the addition was complete, the reaction mixture was stirred at the same temperature until tests for chloride (Volhard) and epoxy groups were negative (nine hours). The product, purified by exposure to a vacuum, was 38.3 g (89.9%) of tris(2,3-dichloropropoxy)methylsilane, n_D^{20} 1.4906; d_4^{20} 1.1452.

	Found %:	C 28.49;	H 4.30;	Si 6.22;	Cl 49.18
$C_{10}H_{18}O_3SiCl_6$.	Calculated %:	C 28.11;	H 4.21;	Si 6.57;	Cl 49.83

Bis(2,3-dichloropropoxy)dimethylsilane. This substance was prepared in a similar way from 28.8 g (0.3 mole) of epichlorohydrin and 19.3 g (0.15 mole) of dichlorodimethylsilane. The addition of dichlorodimethylsilane was spread over three hours; evolution of heat was observed immediately. The mixture was heated at 30-35° for ten hours. Vacuum fractionation then yielded 18.3 g (38.9%) of bis(2,3-dichloropropoxy)dimethylsilane, b.p. 160-165° (37 mm), n_D^{20} 1.4772; d_4^{20} 1.2720.

	Found %:	C 31.94;	H 5.12;	Si 8.20;	Cl 44.07
$C_8H_{16}O_2SiCl_4$.	Calculated %:	C 30.58;	H 5.09;	Si 8.93;	Cl 45.17

(2,3-Dichloropropoxy)trimethylsilane. This substance was prepared in a similar way from 31.4 g (0.33 mole) of epichlorohydrin and 36.1 g (0.33 mole) of chlorotrimethylsilane. Addition of the chlorotrimethylsilane was spread over three hours. The heating was at 30-35° for ten hours. Vacuum fractionation of the product yielded 10.2 g (15.3%) of (2,3-dichloropropoxy)trimethylsilane, b.p. 96-100° (66 mm), n_D^{20} 1.4456; d_4^{20} 1.1094.

	Found %:	C 35.83; H 7.16; Si 13.27; Cl 35.50
$C_6H_{14}OSiCl_2$.	Calculated %:	C 35.82; H 6.96; Si 13.76; Cl 35.27

Bis(2,3-dichloropropoxy)methylsilane. This substance was prepared in a similar way from 37.0 g (0.4 mole) of epichlorohydrin and 23.0 g (0.2 mole) of dichloromethylsilane. Addition of the dichloromethylsilane was spread over three hours; much heat was evolved. Heating was at 30-35° for ten hours. Vacuum fractionation of the product yielded 26.0 g (43.3%) of bis(2,3-dichloropropoxy)methylsilane, b.p. 173-175° (34 mm), n_D^{20} 1.4780; d_4^{20} 1.3740.

	Found %:	C 29.34; H 5.66; Si 8.95; Cl 47.23
$C_7H_{14}O_2SiCl_4$.	Calculated %:	C 28.01; H 4.68; Si 9.35; Cl 47.23

Tris(2,3-dichloropropoxy)ethylsilane. This substance was prepared in a similar way from 27.7 g (0.3 mole) of epichlorohydrin and 16.4 g (0.1 mole) of trichloroethylsilane. Addition of trichloroethylsilane was spread over 2 hours 30 minutes; heat was evolved. The further heating of the reaction mixture was at 38-40° for ten hours. The product was exposed to a vacuum to remove unchanged reactants, and 38.8 g (88.1%) of tris(2,3-dichloropropoxy) ethylsilane, n_D^{20} 1.4880; d_4^{20} 1.3740, was obtained.

	Found %:	C 30.31; H 5.00; Si 5.58; Cl 48.26
$C_{11}H_{20}O_3SiCl_6$.	Calculated %:	C 29.94; H 4.53; Si 6.36; Cl 48.25

Bis(2,3-dichloropropoxy)diethylsilane. This substance was prepared in a similar way from 27.7 g (0.3 mole) of epichlorohydrin and 23.5 g (0.15 mole) of dichlorodiethylsilane. Addition of dichlorodiethylsilane was spread over three hours; heat was evolved. The reaction mixture was then stirred at 40-50° for ten hours. Vacuum distillation yielded 5.2 g (10.1%) of bis(2,3-dichloropropoxy)diethylsilane, b.p. 150-200° (36 mm), n_D^{20} 1.4815.

	Found %:	C 34.21; H 6.09; Si 7.95; Cl 41.68
$C_{10}H_{21}O_2SiCl_4$.	Calculated %:	C 35.10; H 5.84; Si 8.21; Cl 41.47

(2,3-Dichloropropoxy)triethylsilane. This substance was prepared in a similar way from 18.5 g (0.2 mole) of epichlorohydrin and 30.1 g (0.2 mole) of chlorotriethylsilane. Addition of the chlorotriethylsilane was carried out at 40-50° and was spread over 90 minutes. The reaction mixture was then stirred at 40-50° for ten hours. Vacuum distillation yielded 15.8 g (32.6%) of (2,3-dichloropropoxy)triethylsilane, b.p. 65-70° (100 mm), n_D^{20} 1.4492; d_4^{20} 1.0776.

	Found %:	C 45.27; H 9.40; Si 11.60; Cl 30.22
$C_9H_{20}OSiCl_2$.	Calculated %:	C 44.53; H 8.22; Si 10.90; Cl 29.18

Bis(2,3-dichloropropoxy)ethylsilane. This substance was prepared in a similar way from 37.0 g (0.4 mole) of epichlorohydrin and 25.8 g (0.2 mole) of dichloroethylsilane. The reaction mixture was stirred at 30-35° for twelve hours. Vacuum distillation of the product yielded 46.7 g (74.5%) of bis(2,3-dichloropropoxy)ethylsilane, b.p. 185-190° (34 mm), n_D^{20} 1.4790; d_4^{20} 1.2992.

	Found %:	C 30.21; H 5.40; Si 8.83; Cl 45.17
$C_8H_{16}O_2SiCl_4$.	Calculated %:	C 30.58; H 5.09; Si 8.93; Cl 45.16

Tris(2,3-dichloropropoxy)phenylsilane. This substance was prepared in a similar way from 36.0 g (0.3 mole) of epichlorohydrin and 27.4 g (0.1 mole) of trichlorophenylsilane. Addition of the trichlorophenylsilane was spread over 90 minutes; heat was evolved. The reaction mixture was then stirred at 40-45° for 18 hours. The product was exposed to a vacuum to remove unchanged reactants, and 43.1 g (67.9%) of tri(2,3-dichloropropoxy)phenylsilane, n_D^{20} 1.5247; d_4^{20} 1.3666.

	Found %:	C 37.00; H 3.90; Si 5.96; Cl 44.74
$C_{15}H_{20}O_3SiCl_6$.	Calculated %:	C 36.92; H 3.70; Si 5.74; Cl 44.51

Tetrakis(2,3-dichloropropoxy)silane. This substance was prepared in a similar way from 37 g (0.4 mole) of epichlorohydrin and 17 g (0.1 mole) of silicon tetrachloride. Reaction was rather violent, and the silicon tetrachloride was added slowly, over a period of six hours, at 35-40°. The reaction mixture was then stirred at this temperature for twelve hours. The product was exposed to a vacuum to remove unchanged reactants, and 48.7 g (89.4%) of tetrakis(2,3-dichloropropoxy)silane, n_D^{20} 1.5017; d_4^{20} 1.4590, was obtained. It was not found possible to prepare this substance in an adequately pure form.

Found %: C 27.37; H 4.06; Si 5.14; Cl 51.94

$C_{12}H_{24}O_4SiCl_2$. Calculated %: C 26.68; H 3.71; Si 5.19; Cl 52.55

4. Reactions of Glycidol with Organochlorosilanes

(2-Chloro-3-hydroxypropoxy)trimethylsilane (2-Chloro-3-trimethylsilyloxy)-1-propanol). Glycidol (16.2 g, i.e. 0.2 mole) was placed in a three-necked flask fitted with stirrer, thermometer, and dropping funnel, and protected with a calcium chloride tube. The glycidol was stirred, and 21.7 g (0.2 mole) of chlorotrimethylsilane was added with cooling to maintain the temperature at 25-28°. When the addition was complete the mixture was heated at 40-50° until test for chloride ions and epoxy groups were negative (two hours). Vacuum distillation of the product yielded 35 g (99%) of (2-chloro-3-hydroxypropoxy)trimethylsilane, b.p. 82-84° (18 mm), n_D^{20} 1.4443; d_4^{20} 1.1331. The purification and identification of products formed by reaction with glycidol were made difficult by the occurrence of a feeble side reaction between the chlorine atoms of the organochlorosilanes and the hydroxyl of glycidol.

Found %: C 40.4; H 8.5; Si 14.9; Cl 19.4; OH 8.9

$C_6H_{15}O_2SiCl$. Calculated %: C 39.43; H 8.28; Si 15.39; Cl 19.41; OH 9.31

Bis(2-Chloro-3-hydroxypropoxy)dimethylsilane (3,3'-(Dimethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 32.4 g (0.4 mole) of glycidol and 25.6 g (0.2 mole) of dichlorodimethylsilane. Yield 55 g (99%), b.p. 108° (20 mm), n_D^{20} 1.4720; d_4^{20} 1.2267.

Found %: C 34.8; H 6.6; Si 8.8; Cl 25.6; OH 11.7

$C_8H_{18}O_4SiCl_2$. Calculated %: C 34.64; H 6.54; Si 10.10; Cl 25.57; OH 12.27

Tris(2-chloro-3-hydroxypropoxy)methylsilane (3,3',3''-(Methylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared in a similar way from 24.3 g (0.3 mole) of glycidol and 15.0 g (0.1 mole) of trichloromethylsilane. Yield 27 g (75%), b.p. 97° (16 mm), n_D^{20} 1.4837; d_4^{20} 1.3219.

Found %: C 32.6; H 5.9; Si 6.9; Cl 28.7; OH 13.8

$C_{10}H_{21}O_6SiCl_3$. Calculated %: C 32.29; H 5.69; Si 7.54; Cl 28.62; OH 13.72

Bis(2-chloro-3-hydroxypropoxy)methylsilane (3,3'-(Methylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 11.6 g (0.1 mole) of dichloromethylsilane. Yield 25 g (95%), n_D^{20} 1.4725. Owing to its high viscosity, this product—and also all those described below—were not distilled, but were exposed to a vacuum for two hours at 20° before being analyzed.

Found %: C 31.4; H 6.2; Si 9.3; Cl 26.5; OH 13.1

$C_7H_{16}O_4SiCl_2$. Calculated %: C 31.93; H 6.09; Si 10.64; Cl 26.99; OH 12.92

Bis(2-chloro-3-hydroxypropoxy)diethylsilane (3,3'-(Diethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 15.6 g (0.1 mole) of dichlorodiethylsilane. Yield 30 g (98%), n_D^{20} 1.4770; d_4^{20} 1.2063.

Found %: C 40.0, H 7.9; Si 8.9; Cl 22.7; OH 12.0

$C_{10}H_{22}O_4SiCl_2$. Calculated %: C 39.33; H 7.26; Si 9.17; Cl 23.24; OH 11.14

Tris(2-chloro-3-hydroxypropoxy)ethylsilane (3,3',3''-(Ethylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared in a similar way from 24.3 g (0.3 mole) of glycidol and 16.3 g (0.1 mole) of trichloroethylsilane. Yield 24 g (62%), n_D^{20} 1.4880; d_4^{20} 1.3142.

Found %: C 34.1; H 6.6; Si 7.5; Cl 26.6; OH 12.4

$C_{11}H_{23}O_6SiCl_3$. Calculated %: C 34.24; H 6.02; Si 7.26; Cl 27.58; OH 13.22

Bis(2-chloro-3-hydroxypropoxy)ethylsilane (3,3'-Ethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 12.9 g (0.1 mole) of dichloroethylsilane. Yield 25 g (93%); n_D^{20} 1.4810.

Found %: C 34.8; H 6.5; Si 9.8; Cl 24.8; OH 12.5

$C_8H_{18}O_4SiCl_2$. Calculated %: C 34.65; H 6.54; Si 10.10; Cl 25.59; OH 12.27

Tris(2-chloro-3-hydroxypropoxy)phenylsilane (3,3',3''-Phenylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared similarly from 16.2 g (0.2 mole) of glycidol and 13.9 g (0.066 mole) of trichlorophenylsilane. Yield 24 g (85%), n_D^{20} 1.5210; and d_4^{20} 1.3256.

Found %: C 40.0; H 6.0; Si 5.9; Cl 24.4; OH 12.5

$C_{15}H_{23}O_6SiCl_3$. Calculated %: C 41.51; H 5.34; Si 6.45; Cl 23.34; OH 12.57

Tetrakis(2-chloro-3-hydroxypropoxy)silane. This substance was prepared similarly from 16.2 g (0.2 mole) of glycidol and 8.5 g (0.05 mole) of silicon tetrachloride. Yield 15 g (67%) n_D^{28} 1.4925.

$C_{12}H_{24}O_8SiCl_4$. Found %: C 30.8; H 5.6; Si 5.5; Cl 29.2; OH 15.7
Calculated %: C 30.89; H 5.19; Si 6.01; Cl 30.42; OH 14.56

5. Hydrolysis of (2,3-Dichloropropoxy)trimethylsilane and Identification of the Dichloropropanol Formed

a) A mixture of 44 g (0.22 mole) of (2,3-dichloropropoxy)trimethylsilane, 18 g (1 mole) of distilled water, and 1.45 g of hydrochloric acid, sp.gr. 1.17 was prepared in a conical flask fitted with a thermometer and was then shaken continuously for 90 minutes. During the shaking the temperature of the reaction mixture rose to 30-35°, and separation into three layers was observed. After the hydrolysis the reaction mixture was separated in a separating funnel. Distillation of the upper layer yielded 14.5 g (81%) of hexamethyldisiloxane, b.p. 101°. Vacuum distillation of the lower layer yielded 19.5 g (68%) of a dichloropropanol, b.p. 87-88° (5 mm).

b) Dichloropropanol obtained by the hydrolysis of (2,3-dichloropropoxy)trimethylsilane (16 g, i.e. 0.124 mole) was placed in a Claisen flask, and 13 g of distilled water was added.

Freshly calcined calcium oxide (7.8 g) was weighed into a porcelain dish and slaked with 5 g of water. The slaked lime was transferred to the Claisen flask, which was then shaken vigorously until separation of layers occurred (90 minutes). The liquid that separated was distilled, and the distillate, which came over at 62-70° (60 mm), separated into two layers. The lower layer was separated in a separating funnel and distilled at atmospheric pressure. No epichlorohydrin was obtained.

A control experiment was carried out in a similar way with 1, 3-dichloro-2-propanol, and 4.9 g (39.5%) of epichlorohydrin (b.p. 115-118°; epoxy content 43.3%) was obtained.

SUMMARY

1. The reaction of epichlorohydrin with organochlorosilanes leads to the formation of alkyl (2,3-dichloropropoxy)silanes. Ten new compounds of general formula

$$R_nSi(OCH_2-\underset{Cl}{CH}-CH_2Cl)_{(4-n)}.$$

(R = CH_3, C_2H_5, C_6H_5) were synthesized, and their properties were studied.

2. Glycidol reacts with organochlorosilanes with participation of the epoxide ring, which is opened. Under the conditions described, the hydroxyl group either does not react, or reacts only to a slight extent. Nine new compounds were synthesized from glycidol and organochlorosilanes, their general formula being

$$R_nSi(OCH_2CHCl-CH_2OH)_{(4-n)}.$$

3. It was established that in the reaction of unsymmetrical α-epoxides with organochlorosilanes opening of the epoxide ring proceeds according to the scheme:

$$R_3SiCl + \underset{\diagdown O \diagup}{CH_2-CH}-CH_2Cl \rightarrow R_3Si-OCH_2-\underset{Cl}{CH}-CH_2Cl$$

LITERATURE CITED

[1] R. Sauer, W. Patnode, J. Am. Chem. Soc. 67, 1548 (1945).

[2] W. Gilliam, R. Meals, R. Sauer, J. Am. Chem. Soc. 68, 1161 (1946).

[3] German Pat. 802895, 803079, and others.

[4] U. S. Pat. 2389802.

[5] K. Michael, Ber. 39, 2789 (1906).

[6] Organic Syntheses, Collected Vol. 2, Foreign Lit. Press, Moscow, 1949, p. 573.

[7] Organic Syntheses, Collected Vpl. 1, Foreign Lit. Press, Moscow, 1949, p. 213.

[8] I. Houben, Methods of Organic Chemistry, Vol. 3, Part 1, United Sci. Tech. Press, Moscow and Leningrad, (Trans) 1934, p. 252.

Received May 13, 1954

V. I. Lenin Electrotechnics Institute

BLANK
PAGE

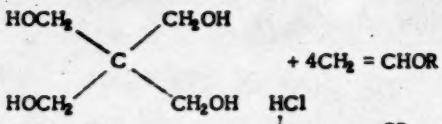
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

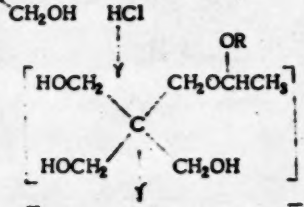
COMMUNICATION 6. REACTION OF VINYL ETHERS WITH PENTAERYTHRITOL

M. F. Shostakovsky, A. S. Atavin, and V. V. Zhebrovsky

We have shown previously that vinyl ethers react with glycols [1, 2], glycerol [3, 4], and polyvinyl alcohol [5] with formation of cyclic acetals. By the reaction of glycerol with vinyl ethers under various conditions we have prepared partial cyclic acetals, diglycerol triacetal, and mixed cyclic acetals containing an O-(1-alkoxyethyl) group. It was of interest in this connection to investigate the reactions of vinyl ethers with polyhydric alcohols containing even numbers of hydroxyls, such as pentaerythritol, the conditions being then favorable for the formation of full cyclic acetals.

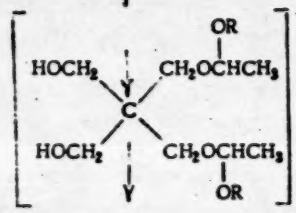
In the reaction of vinyl ethers with pentaerythritol, it might be expected that the process would at first take the following directions:



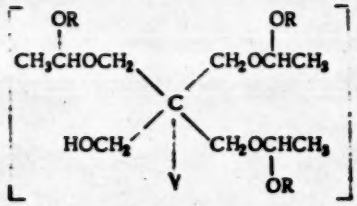


(I)

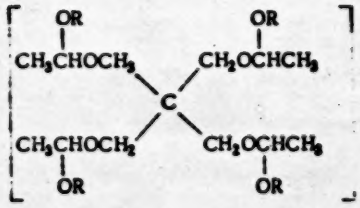
(R = C_2H_5, C_4H_9).



(II)



(III)

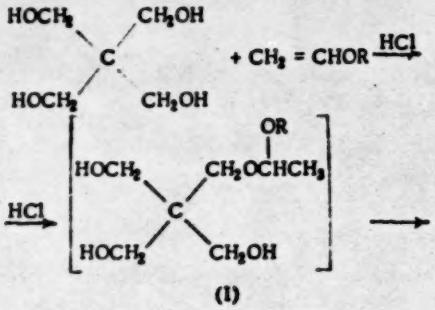


(IV)

This should lead to the formation of mixed acetals of pentaerythritol with monohydric alcohols in a series of increasing degree of substitution, (I), (II), (III), and (IV). In the present investigation, however, none of these acetals was isolated.

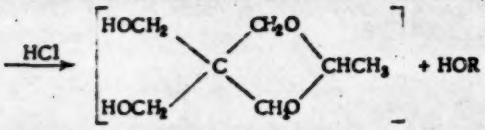
On the basis of our previous investigations and of the experimental results of the present investigation, it is more probable that reaction of alkyl vinyl ethers with pentaerythritol, which leads finally to the formation of

the bicyclic acetal of pentaerythritol, proceeds according to the following scheme:



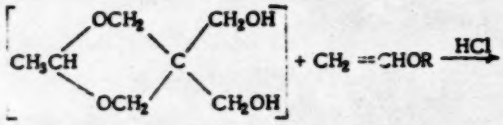
(I)

(R = C_2H_5, C_4H_9)

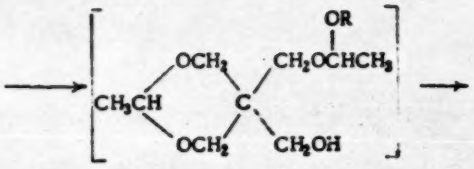


(V)

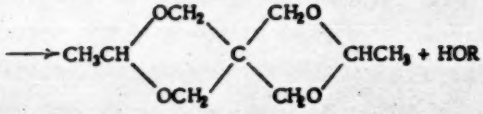
The partial acetal of pentaerythritol (I) is formed at first, and this is then converted into the cyclic acetal (V) with elimination of monohydric alcohol. The partial cyclic acetal of pentaerythritol then reacts with another molecule of alkyl vinyl ether with formation of the mixed acetal (VI), which is converted into the bicyclic acetal of pentaerythritol (VII) in accordance with the following scheme:



(V)



(VI)



(VII)

In the course of the investigation we have isolated the bicyclic acetal of pentaerythritol (VII), the acetaldehyde dialkyl acetals, and the alcohols themselves. It is clear that the formation of the dialkyl acetals in the synthesis of the bicyclic acetal of pentaerythritol (VII) results mainly from the reaction of the vinyl ethers with alcohols eliminated in the cyclization reactions. The present investigation shows that the bicyclic acetal (VII) is formed with various proportions of reactants, including those in which the vinyl ether is in excess. The pentaerythritol acetal (VII) was prepared by Nieuwland [6] by the action of acetylene on pentaerythritol in presence of mercuric oxide and boron trifluoride.

It may probably be assumed that in the formation of the bicyclic acetal of pentaerythritol (VII) cyclization of the mixed acetal (I) and later of the acetal (VI) proceeds more rapidly than the addition of alkyl vinyl ether to all four hydroxyls of the pentaerythritol. As already pointed out, in the synthesis of the bicyclic acetal (VII) a monohydric alcohol is elminated, and this reacts with free alkyl vinyl ether with formation of the corresponding acetal.

Thus, part of the vinyl ether is consumed in the formation of the dialkyl acetal, and it was found that the highest yield of the bicyclic acetal of pentaerythritol (VII) was obtained when excess of the alkyl vinyl ether was used.

EXPERIMENTAL

For the synthesis of the acetals the following substances were used: ethyl vinyl ether, b.p. 35.9°, d_4^{20} 0.7533; n_D^{20} 1.3778; butyl vinyl ether, b.p. 93.7-93.8°, d_4^{20} 0.7791; n_D^{20} 1.4029; and pentaerythritol, m.p. 253°.

a) Reaction of Ethyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 7.1 : 1. A mixture of 20 g of pentaerythritol and 75.3 g of ethyl vinyl ether was prepared in a flask fitted with mercury-sealed stirrer, reflux condenser, and thermometer, and six drops of hydrochloric acid (0.084 g of HCl) were added; the temperature of the reaction mixture rose to 78°. The reaction product, which was dark in color, was neutralized with potassium carbonate and fractionated from a Favorsky flask under reduced pressure, when the following fractions were obtained:

Frac. I	b.p. to 33° (35 mm);	4.5 g
Frac. II	b.p. to 28° (22 mm);	9 g
Frac. III	b.p. 106-110° (9 mm);	13 g (solidified)
Residue		65 g (resinous mass)

Fraction I was ethyl alcohol containing some acetaldehyde diethyl acetal. After being redistilled Fraction II boiled at 20° (22 mm) and had n_D^{20} 1.3820, which corresponds to acetaldehyde diethyl acetal (the literature [7] gives n_D^{20} 13820). After being recrystallized from alcohol Fraction III melted at 40°; its molecular weight, determined cryoscopically in benzene, was M 186 (calculated for $C_9H_{16}O_4$, M 188).

Found %:	C 57.76; 57.67;	H 8.23; 8.50
Calculated %:	C 57.42;	H 8.56

The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

b) Reaction of Butyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 2.24 : 1. Pentaerythritol (20 g) and butyl vinyl ether (32.8 g) were stirred together in a flask for ten minutes, and 15 drops of hydrochloric acid (0.210 g of HCl) were added. The temperature of the reaction mixture rose spontaneously to 72°, when the liquid boiled; the temperature rose further to 128°.

Some precipitate was present, and was separated, washed with acetone, and dried. It was found to be pentaerythritol.

After being neutralized with potassium carbonate, the liquid was fractionated, the following fractions being obtained:

Frac. I,	b.p. 117-122°	11 g;	n_D^{20} 1.3997
Frac. II,	b.p. 58-65° (for 7 mm);	10 g;	n_D^{20} 1.4096
Frac. III,	b.p. 98-106° (for 7 mm);	13 g;	
	Residue	10 g	

After being redistilled Fraction I boiled at 117-118.5° and had n_D^{20} 1.3990 and d_4^{20} 0.8105. These constants correspond to butyl alcohol, for which the literature [8] gives b.p. 117-118° and n_D^{20} 1.3983. The yield of butyl alcohol was 9.6 g.

Fraction II was redistilled and then had b.p. 60-61° (7 mm), n_D^{20} 1.4090, and d_4^{20} 0.8269. These constants correspond to acetaldehyde dibutyl acetal, for which the literature [9] gives n_D^{20} 1.4090 and d_4^{20} 0.8267. The yield was 8 g.

Fraction III solidified when allowed to stand. After being recrystallized from alcohol it melted at 40°. Found M 186 (cryscopically in benzene); for $C_9H_{16}O_4$ calculated M 888. The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

c) Reaction of Butyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 5.2 : 1. Pentaerythritol (20 g) and butyl vinyl ether (76.4 ml) were stirred together in a flask for 30 minutes, and 15 drops of hydrochloric acid (0.21 g of HCl) were added; the temperature rose to 130°. The reaction mixture was an oily mass that darkened in the air. It was neutralized with potassium carbonate and distilled, when the following fractions were obtained:

Frac. I,	b.p. 116-125°;	12 g
Frac. II,	b.p. 58-62 (for 7 mm);	20 g
Frac. III,	b.p. 98-110° (for 7 mm);	29 g
	Residue 33 g	

Redistillation of Fraction I yielded 10 g of a substance boiling at 117-118° and having n_D^{20} 1.3992, corresponding to butyl alcohol.

After being refractionated Fraction II had b.p. 60-61° (7 mm), n_D^{20} 1.4099, and d_4^{20} 0.8269, corresponding to acetaldehyde dibutyl acetal.

Crystallization of Fraction III from alcohol yielded 21 g of a crystalline substance, m.p. 40°. Found M 187; Found M 187; for $C_9H_{18}O_4$ calculated M 186. The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

SUMMARY

1. The reactions of alkyl vinyl ethers (the ethyl and butyl ethers) with pentaerythritol were studied for various proportions of the reactants.

2. It was shown that an alkyl vinyl ether reacts with pentaerythritol in presence of hydrochloric acid with formation of the bicyclic acetal of pentaerythritol, the dialkyl acetal of acetaldehyde, and the monohydric alcohol.

LITERATURE CITED

[1] M. F. Shostakovsky, N. A. Gershtein, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No 4, 671.•

[2] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No 4, 683.••

[3] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No 1, 166.•••

[4] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No 2, 354.••••

[5] M. F. Shostakovsk V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No 3, 535. •••••

[6] J. A. Nieuwland, R. R. Vogt, H. Foohey, J. Am. Chem. Soc. 1018, (1930).

[7] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, 1952, p. 203.

[8] Short Handbook of Chemistry, 1951, p. 166.

[9] M. F. Shostakovsky and N. A. Gershtein. J. Gen. Chem. 16, 6, 937(1946).

Received January 27, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

• Consultant's Bureau Translation, p 617.
•• Consultant's Bureau Translation, p 583.
••• Consultant's Bureau Translation, p 137.
•••• Consultant's Bureau Translation, p 317.
••••• Consultant's Bureau Translation, p 455.

OPTICAL INVESTIGATION OF SOME VINYL ETHERS OF ETHANOLAMINES

M. F. Shostakovsky, M. I. Batuev, I. A. Chekulaeva, and A. D. Matveeva

Chemical and optical investigations of monovinyl ethers of glycols and polyethylene glycols have shown that the chemical inertness of these substances in several reactions that are characteristic of vinyl ethers [1] is to be explained by the formation of intermolecular hydrogen bonds, which "block" the hydrogen of the hydroxyl group [2]. As is well known, hydrogen bonds of the types N – H....O, O – H....N, and N – H...N occur in compounds of various kinds (amines, amides, etc.), and their presence has been confirmed optically, like that of the hydrogen bond of the type O – H...O in aliphatic alcohols, aliphatic acids, monovinyl ethers of glycols and polyethylene glycols, etc. The observed chemical inertness of vinyl ethers of ethanolamines ($CH_2 = CHOCH_2CH_2NH_2$, $CH_2 = CHOCH_2CH_2NHR$) has led us to assume that hydrogen bonds of the types N – H...O and N – H...N are formed in these compounds.

The fact that it has not been found possible to bring about the addition of alcohols to vinyl ethers of ethanolamines and to effect their cyclization and polymerization in presence of ionic catalysts is to be explained by the presence of a hydrogen bond, associated with the ability of nitrogen to give onium compounds. On the other hand, vinyl ethers of ethanolamines whose structures preclude the formation of hydrogen bonds ($CH_2 = CHOCH_2CH_2NR_2$) do not show this chemical inertness [3]. These considerations prompted us to make a special investigation of some vinyl ethers of ethanolamines with the object of determining what hydrogen bonds were present.

We investigated:

The vinyl ether of 2-aminoethanol $CH_2 = CHOCH_2CH_2NH_2$ (I)

The divinyl ether of diethanolamine $(CH_2 = CHOCH_2CH_2)_2NH$ (II)

The methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid $CH_2 = CHOCH_2CH_2NHCH_3OCOCH(CH_3)CH_2$ (III)

The vinyl ether of 2-anilinoethanol $CH_2 = CHOCH_2CH_2NHC_6H_5$ (IV)

Monoethanolamine (2-aminoethanol) (taken for optical comparison) $HOCH_2CH_2NH_2$ (V)

The vinyl ether (I), (II), and (IV) were prepared by the vinylation of the corresponding amino alcohols [3, 4], and the vinyl ether (III) was prepared by reaction of the vinyl ether of 2-aminoethanol with methyl methacrylate [5]. The constants of these compounds are given in Table 1.

It was natural to turn first to the cryoscopic determination of the degree of association of the vinyl ethers of ethanolamines. We carried out this determination for three of the ethers in benzene solution; 2-aminoethanol is insoluble in benzene. The results of the determination are given in Table 2. They show that, even in solutions of fairly high concentration, the degree of association of these ethers is close to unity.

We may infer from this that vinyl ethers of ethanolamines do not tend to form long associated chains or cyclic dimer complexes (schemes (a) and (b)) to any appreciable extent. If a hydrogen bond is formed in these compounds, then it can only be an intramolecular bond (scheme (c)). The cryoscopic results, however, cannot in themselves answer the question of whether such an intramolecular hydrogen bond exists in these ethers, or whether it is in general absent. Suitable optical investigations (by Raman spectra) can answer this question.

In the liquid phase compounds containing amino (NH_2) and imino (NH) groups are generally associated by means of hydrogen bonds (N – H...N, or N – H...O, if the compound also contains oxygen). The participation of N – H in a hydrogen bond is manifested optically by a lowering of the vibrational frequency of the N – H bond. Lines corresponding to these frequencies are not smeared out into wide continuous bands (as for methyl

and ethyl alcohols and for monovinyl ethers of glycols and polyethylene glycols, but are only broadened somewhat. The most intense of these form broad lines, sometimes almost narrow bands •.

TABLE 1

Physical Constants of Vinyl Ethers of Ethanolamines, and also of 2-Aminoethanol

Compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
Vinyl ether of 2-aminoethanol. . . .	115-116 (735)	1.4390	0.9018
Divinyl ether of diethanolamine. . .	68-69 (3.5)	1.4576	0.9491
Methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid.	97.5 (4)	1.4491	0.9998
Vinyl ether of 2-anilinoethanol. . . .	108-109 (35)	1.5523	1.0295
2-Aminoethanol.	169-170	1.4555	1.013

TABLE 2

Cryoscopic Determination of the Degree of Association of Vinyl Ethers of Ethanolamines in Benzene Solution

Vinyl ether of 2-aminoethanol		Divinyl ether of diethanolamine		Vinyl ether of 2-anilinoethanol	
Concentration (mole-%)	Degree of association	Concentration (mole-%)	Degree of association	Concentration (mole-%)	Degree of association
0.865	1.015	0.4075	1.000	2.216	0.9934
1.275	1.109	1.5475	1.000	4.277	1.037
3.724	1.140	3.1150	1.000	6.988	1.073
5.457	1.169	6.2710	1.036	9.739	1.085
13.450	1.306	8.0940	1.054	16.16	1.178
20.92	1.396	16 970	1.073	–	–
–	–	24.95	1.161		–

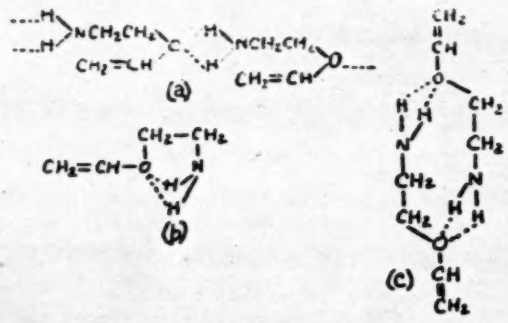
Possible Kinds of Hydrogen Bonds in Vinyl Ethers of Ethanolamines

(a) Association into long chains

(b) Association into a cyclic dimer

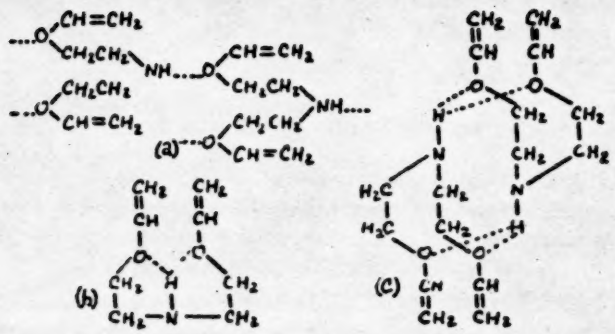
(c) Intramolecular hydrogen bond

Vinyl Ether of 2-Aminoethanol (I)

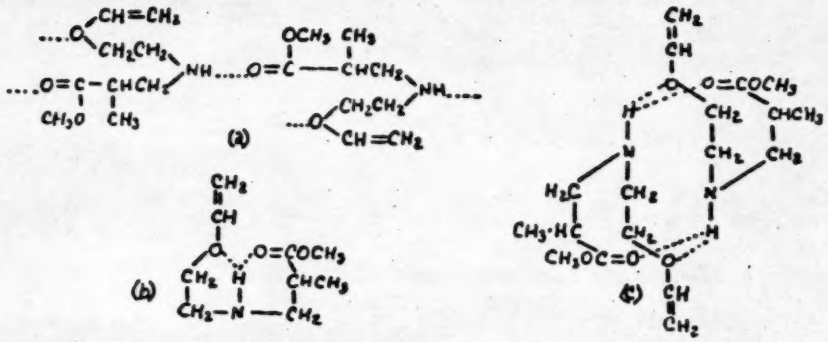


• The main optical criteria of the participation of the O – H group in a hydrogen bond are a displacement in the direction of the longer waves and an appearance of a set of frequencies in the region that is characteristic for the hydroxyl group. The smearing out of these frequencies in the liquid phase into a wide continuous band is due to various disturbances in short-range order in the liquid (quasi-crystalline) state of matter, and not to the formation of a hydrogen bond, as such; it is a secondary effect of hydrogen bonding found in the liquid phase [6]. When NH_2 or NH groups participate in hydrogen bonding, this secondary effect is found only rarely.

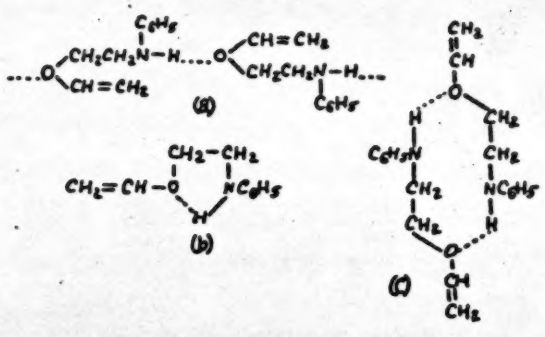
Divinyl Ether of Diethanolamine (II)



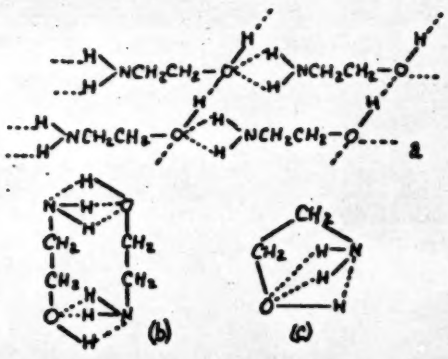
Methyl Ester of 2-Methyl-3-[(2-vinyloxyethyl)amino]propionic Acid (III)



Vinyl Ether of 2-Anilinoethanol (IV)



2-Aminoethanol (V)



In Table 3, by way of example, we show the lowering of the vibrational frequencies of the N − H bond for several compounds as we pass from the gas phase (isolated molecules) to the liquid phase (molecules associated by means of the hydrogen bond N − H...O or N − H...N). Table 3 shows that the frequency of the N − H bond in isolated molecules lies in a fairly high region − about 3500 cm^{-1} and even higher (vibrations of the imino group and asymmetrical vibrations of the amino group).

2-Aminoethanol, which we investigated optically for purposes of comparison, is insoluble in benzene. This fact is an indication that forms very powerful intermolecular hydrogen bonds (type (a) reather than type (b)) which are not broken down by benzene. If there were an intermolecular hydrogen bond of type (c), or even a cyclic dimer of type (b), it would be expected that the substance would be readily soluble in benzene. In 2-aminoethanol, but not in vinyl esters of ethanolamines, O − H...O bonding is possible as well as N − H...O. The O − H...O linkage is evidenced by a characteristic highly diffuse band in the region 3150-3400 cm^{-1}, which forms a background to the system of bands of the NH_2 group participating in the N − H...O linkage. This system of frequencies is distributed over the range 3145-3364 cm^{-1} (see Column V in Table 4), i.e. in the same range as that of the frequencies of the associated molecules of the compounds listed in Table 3.

TABLE 3

Vibrational Frequencies of the N − H Bond of Certain Compounds in the Gas and Liquid Phases [7]

Compound	Vibrational frequencies (cm^{-1})	
	Gas phase	Liquid phase
HNCO	3531	3133
$HCONH_2$	3533 (a) 3411 (s)	3499, 3307, 3228, 3176
CH_3CONH_2	3533(a), 3415 (s)	3501, 3351, 3190
$C_2H_5OOCNH_2$	3557 (a) 3442 (s)	3513, 3324, 3226, 3176

(a) - asymmetrical frequency; (s) - symmetrical frequency

TABLE 4

Frequencies of the N − H Bonds of the Vinyl Ethers of Ethanolamines (I), (II), (III), and (IV) and of 2-Aminoethanol (the vinyl ethers (I), (II), (III), and (IV) are given in the same order as before)

I	II	III	IV	V
–	–	–	–	3145 (1)
–	–	3176 (1)	–	3187 (3)
3217 (0)	3225 (0)	3224 (1)	–	–
–	–	–	–	3239 (2)
3263 (1)	3271 (1)	3274 (1)	–	–
3293 (1)	–	–	–	–
–	–	–	3301 (1)	3300 (6b)
3324 (5b)	3338 (4b)	3343 (4b)	–	–
–	–	–	3351 (1)	–
–	–	–	–	3364 (3b)
3385 (3b)	–	–	–	–
–	–	–	3406 (4b)	–

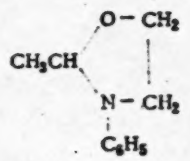
For the vinyl ethers of ethanolamines (I), (II), (III), and (IV) (Table 4) we again observe the system of frequencies in the same longer-wave region for N − H bonds taking part in the hydrogen bond N − H...O, and the intense lines of this system are again broadened appreciably. This displacement of the system of N − H frequencies in the direction of longer wave s, as compared with the frequencies of these bonds in monomeric molecules (Tables 3 and 4) is an indisputable proof of the presence of hydrogen bonds in these compounds. Taking into account the cryoscopic data given above, we must conclude that in these compounds ((I), (II), (III), (IV)) intramolecular hydrogen bonding is overwhelmingly predominant ((Ic), (IIc), (IIIc), and (IVc)). It should be noted that a certain simplification of the system of N − H frequencies in (II), (III), and (IV), as compared with (I) and (V) (fewer intensive lines − one, instead of two or three), is to be attributed to the replacement of a hydrogen atom of the

amino group by a radical.

Hence, the higher reactivity that we have observed in those vinyl ethers of ethanolamines whose structures clearly exclude the possibility of hydrogen bonding together with the results of the optical investigation of four chemically inert ethers that form intramolecular hydrogen bonds show that the chemical inertness of the investigated vinyl ethers of ethanolamines, like that of monovinyl ethers of glycols and polyethylene glycols [2], is associated with the occurrence of hydrogen bonding. The hydrogen bonding in vinyl ethers of ethanolamines, however, unlike that in the glycol vinyl ethers, is undoubtedly mainly intramolecular, not intermolecular.

By varying the substituent on the nitrogen in vinyl ethers of ethanolamines, we may alter the strength of the intramolecular hydrogen bond — and therefore the reactivity — and follow this alteration optically. Thus, in the divinyl ether of diethanolamine (II) and the methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid (III) the >NH group is more strongly drawn into the hydrogen bond as a result of the participation of the two oxygen atoms present in these compounds (IIc and IIIc) in the formation of the bond. The strengthening of the hydrogen bond is manifested by a lowering of the whole system of N — H frequencies in (II) and (III), as compared with (I) and (IV) (Table 4). For this reason, the vinyl ethers (II) and (III) differ little in their chemical inertness in reactions characteristic for vinyl ethers from the vinyl ether of 2-aminoethanol (I); they are extremely inert chemically.

However, when one hydrogen of the vinyl ether (I) is replaced by phenyl, notable changes in the chemical and optical behavior of the compound are to be observed. Thus, in contrast with (II) and (III), the compound (IV) has an N — H frequency system (Table 4) that is raised throughout, as compared with the system of (I) and (V); in particular, the high-frequency limit of the region is raised to 3406 cm^{-1}. Introduction of the phenyl radical raises the energy of the N — H bond, and there is an associated rise in the vibrational frequency. As a result NH...O hydrogen bonds are somewhat weakened, and this in its turn leads to enhanced reactivity in the vinyl ether (IV), as compared with (I), (II), and (III). Unlike the latter, the vinyl ether of 2-anilinoethanol (IV) is readily cyclized, for example in the presence of traces of concentrated hydrochloric acid, with formation of

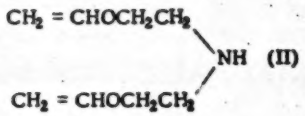


and it also undergoes other reactions [3].

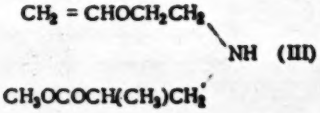
We give below the complete Raman spectra of the investigated compounds (I), (II), (III), (IV), and (V). The spectra were measured with a Soviet spectrograph ISP-51 with the medium camera.

$CH_2 = CHOCH_2CH_2NH_2$ (I)

$\Delta\nu$ cm^{-1}: 169(2), 248 (4b), 265(0), 324(2)•, 352(2)•, 404(1), 435(1), 498(4), 603(3), 644(0), 710(2), 821(5b), 904(4), 966(4), 996(4), 1084(2)•, 1099(3)•, 1113(3)•, 1157(1), 1179(2)•, 1209(2)•, 1321(10), 1354(2), 1407(2), 1461(5), 1617(8), 1637(7), 2871(7), 2932(8b), 3018(3), 3217(0), 3263(1), 3293(1), 3324(5b), 3385(3b).



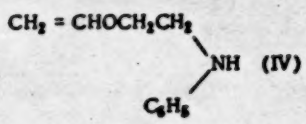
$\Delta\nu$ cm^{-1}: 171(2), 241(4b), 503(3), 609(3), 660(0), 745 (0), 778(0), 826(5b), 892(3), 935(0), 972(3)•, 1001(2)•, 1032(3)•, 1067(2)•, 1102(2)•, 1149(3)•, 1203(3), 1263(3), 1322(10), 1364(0), 1389(1), 1413(2), 1463(3), 1617(8), 1642(7), 2842(2)•, 2876(7)•, 2938(8b)•, 3022(4), 3225(0), 3271(1), 3338(4b).



$\Delta\nu$ cm^{-1}: 163(1), 188(1), 236(3b), 324(1), 366(1), 431(0), 468(0), 505(1b), 611(0b), 658(0b), 708(1), 768(1),

• On a background.

813(1), 838(6b), 903(2b), 935(0), 973(3), 991(3), 1029(0), 1056(0), 1104(1), 1152(1b), 1206(1b), 1321(10), 1366(1), 1419(1), 1463(8), 1619(6), 1637(5), 1660(2), 1698(1), 1737(4), 2880(6)•, 2943(10b)•, 2972(3)•, 3020(2), 3082(0), 3176(1), 3224(1), 3274(1), 3343(4b).



$CH_2 = CHOCH_2CH_2$ \ NH (IV) / C_6H_5

$\Delta\nu cm^{-1}$: 125(2), 178(1), 214(2)•, 233(2)•, 248(2)•, 414(4b), 490(1)•, 510(1)•, 531(1)•, 576(0)•, 596(1)•, 619(4)•, 646(0), 663(0), 752(4), 782(4), 815(5), 833(0), 852(5), 871(0), 916(1), 993(10), 1029(5), 1073(0), 1155(4), 1182(3), 1199(0), 1287(1), 1320(5), 1356(0), 1380(0), 1408(0), 1424(0), 1455(1), 1493(1), 1603(10), 1619(1)•, 1639(1)•, 2850(0), 2876(4), 2931(4), 2984(0), 3024(1), 3301(1), 3351(1), 3406(4b).

$HOCH_2CH_2NH_2$ (V)

$\Delta\nu cm^{-1}$: 171(1), 482(4), 522(2), 838(4), 874(5), 1034(3), 1065(4), 1083(5), 1108(4), 1173(2b), 1248(3b), 1298(5), 1313(5), 1359(4b), 1460(10), 1593(1b)•, 2707(3b)••, 2862(10)••, 2914(9)••, 2942(9)••, 3145(1)•••, 3187(3)•••, 3239(2)•••, 3300(6b)•••, 3364(3b)•••, 3150-3400 (OH band).

• Composite frequency: 482 + 1108 = 1590 (and others).
•• On a background
••• On a background of the OH band.

SUMMARY

1. The Raman spectra were determined for the vinyl ethers of 2-aminoethanol and of 2-anilinoethanol, the divinyl ether of diethanolamine, the methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid, and 2-aminoethanol.

2. It was proved that intramolecular hydrogen bonding occurs in these compounds.

3. It was shown that the chemical inertness of some vinyl ethers of ethanolamines in ionic reactions is associated with the presence of hydrogen bonds in their molecules.

4. A study was made of the dependence of the chemical inertness of vinyl ethers of ethanolamines on their chemical structure, i.e. on the mutual effects of atoms in the molecule.

LITERATURE CITED

[1] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952.

[2] M. F. Shostakovsky, M. I. Batuev, P. V. Tyupaev, and A. D. Matveeva, Proc. Acad. Sci. USSR 89, 93 (1953); 89, 501 (1953); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 1103.

[3] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No 2, 368;• 1954, No.6, 1111; 1955, No 1, 146 ••.

[4] M. F. Shostakovsky, I. A. Chekulaeva, and N. A. Gershtein, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No 3, 328.

[5] M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No 2, 323. •••

[6] M. I. Batuev, J. Phys. Chem, 23, 1399 (1949); 25, 884(1951); Bull. Acad. Sci. USSR, Physical Series 14, 429 (1950).

[7] G. Herzberg, C. Reid, Discussions of the Faraday Society, 1950, No 9, p. 92; M. Davies, J. Evans, J. Chem. Phys. 20, 342 (1952).

• Consultant's Bureau Translation, p335.
•• Consultant's Bureau Translation, p127.
••• Consultant's Bureau Translation, p 263.

Received January 27, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 74. EFFECT OF AROMATIC COMPONENTS ON THE PROPERTIES OF MIXED POLYAMIDES

V. V. Korshak and T. M. Frunze

We have previously described the results of investigations on binary polyamide systems derived from mixtures of various proportions of two 1,6-hexanediamine salts of dicarboxylic acids [1], and also on binary systems derived from a mixture of 6-caprolactam (2-oxohexamethylenimine) and a 1,6-hexanediamine salt of a dicarboxylic acid [2]; various dicarboxylic acids were used. It was found that all the investigated binary systems have a minimum melting point on the "composition—property" graph, and this corresponds to the mixture containing about 60% of the component having the longer molecule [1,2]. When the melting points of single-component polyamides are plotted against the percentage content of amide groupings, the straight line $y = 7x + 110$ is obtained (y is the melting point and x is the mole percentage of hydrogen bonds) [1, 11]. It was found possible, on the basis of this equation, to determine the extent of hydrogen bonding occurring between the macromolecules of a mixed polyamide.

An examination of the mechanism of the formation of mixed polyamides for the case in which one component is 6-caprolactam led to the conclusion that in the first stage simultaneous reactions occur: polymerization of 6-caprolactam by the "hydrolytic-polymerization" mechanism, and polycondensation of the 1,6-hexanediamine salt of the dicarboxylic acid. In the last stage of the process the main direction of the reaction is the polycondensation of polyamide macromolecules formed earlier [2].

The present paper gives the results of an investigation on binary systems in which one component is an aromatic diamine. In order to determine the effect of the presence of an aromatic nucleus on the properties of the polyamide, we have investigated certain binary systems: those derived from one dicarboxylic acid and two diamines (one aliphatic and one aromatic), those derived from two acids and one diamine (aromatic), and finally those derived from two acids and two diamines (one aliphatic and one aromatic). Systems of the first type were prepared from adipic acid, 1,6-hexanediamine, and one of the following aromatic diamines: o-, m-, and p-phenylenediamines and toluene-2,4-diamine. A system of the second type was prepared from sebacic acid, 1,6-hexanediamine, and m-phenylenediamine •. As an example of systems of the third type, polyamides based on adipic and sebacic acids, 1,6-hexanediamine, and m-phenylenediamine were prepared. In addition to these, two multicomponent systems were investigated. Each was based on adipic and sebacic acids, 6-caprolactam, and 1,6-hexanediamine taken in differing but definite proportions, and the adipic or sebacic salt, respectively, of m-phenylenediamine was added in varying amount.

EXPERIMENTAL

Starting Materials

The aromatic diamines were purified by two vacuum distillations in presence of 5-10% by weight of caustic soda, and they were used immediately in the reaction. As aromatic diamines do not give salts with aliphatic dicarboxylic acids, the aromatic diamine and the dicarboxylic acid were taken separately in equivalent amounts.

The following substances were used: toluene-2,4-diamine, b.p. 166° (22 mm) and 175° (28 mm), m.p. 99° (the literature [3] gives b.p. 280° and m.p. 98°); o-phenylenediamine, b.p. 134-136° (3 mm) and 154-156° (6 mm), m.p. 102° (the literature [4, 5] gives b.p. 252-256° and m.p. 102-103.8°); m-phenylenediamine, b.p. 146° (22 mm) and m.p. 62° (the literature [4] gives b.p. 287° and m.p. 62.8°); p-phenylenediamine, b.p. 168° (37 mm) and 267° (atmospheric pressure), m.p. 140° (the literature [6] gives b.p. 267° and m.p. 142° [4]). The characteristics of the remaining monomers and the purification procedures are given in a previous paper [2].

Experimental Procudure

The reactants were introduced into the reaction tubes, which were then evacuated repeatedly and filled

• This system is actually of the first type. No example of the second type of system is discussed in this paper.—Publisher.

with nitrogen in order to remove air as completely as possible and to avoid oxidation of the aromatic amines. In other respects the apparatus, the method of carrying out the reactions, and the methods of determining the properties of the products were as described previously [1,2]. An attempt to prevent contact with air by introducing paraffin into the reaction tubes was not successful. It was thought that paraffin, being of low density, would float on the polyamide and isolate the reaction mass from the air, but it was found that the paraffin readily mixed with the molten polyamide, which formed a spongy mass when cold; also, the paraffin evaporated away to some extent.

TABLE 1

Softening and Melting Points in the System AH-AT

Sample No.	Softening point (°C)	Melting point (°C)
2	110	190-195
3	98	130-133
4	98	128-130
5	115	150-153
6	150	175-178

The products had extended melting ranges. Softening began considerably before the melting point was reached, this point being defined as the temperature at which it becomes possible to draw the substance out into a thread. For comparison purposes softening and melting points are given in Table 1 for products of the system (adipic acid + toluene-2,4-diamine) + 1,6-hexanediamine adipate; in the other tables the figures given are melting points.

Results

Table 2 gives the melting points of the binary polyamides that we prepared.

The products were brittle yellow solids. As the content of aromatic diamine increased, the color deepened from cream or light yellow, in polyamides containing 0.2 of a molecular proportion, to amber brown, in polyamides containing 0.8 of a molecular proportion. At the same time the clarity increased, the products containing up to 0.2 of a molecular proportion of aromatic diamine being opaque, and the remainder quite transparent. All these products gave threads, though those containing more than 0.2 of a molecular proportion of aromatic diamine gave weak, brittle threads; they did not form films.

These polyamides dissolved when heated with cresol, but were insoluble in other organic solvents. Only the system AH-SmP gave some products – those having the lowest melting points – which were soluble in a mixture of alcohol and chloroform, in alcohol, and in 2-methoxyethanol (the solvents are placed in order of diminishing solvent power); they were insoluble in 2-ethoxyethanol.

TABLE 2

Melting Points of Polyamides Prepared from Mixtures Containing Aromatic Diamines

Ratio of original substances*	Original substances**					
	AH / AT	AH / ApP	AH / AoP	AH / AmP	AH / SmP	SH / SmP
1.0 0.0	250-252	250-252	250-252	250-252	250-252	210-212
0.8/0.2	190-195	225-233	205-215	200-210	170-175	150-160
0.6 0.4	130-133	185-195	150-160	170-178	110-115	110-115
0.4 0.6	128-130	136-142	115-125	135-142	115-120	90-100
0.2 0.8	150-153	125-133	90-105	133-140	125-130	85-98
0.0 1.0	175-176	260-262	105-110	258-259	145-150	145-150

We then investigated the effect of additions of various amounts of m-phenylenediamine, together with adipic or sebacic acid, to the ternary mixed polyamide prepared from AH, SH, and 6-caprolactam, two variants of this being used. The first polymer (P_1) was obtained from 40% of AH, 20% of SH, and 40% of 6-caprolactam (by weight). The second polymer (P_2) was prepared from 40% of AH, 40% of SH, and 20% of 6-caprolactam.

The first polymer melted at 145°, and the second at 160°. They were both readily soluble when heated with 85-96% alcohol, and the 15% solutions obtained did not gel in the course of 10-24 hours. P_1 and P_2 were white

* The numerator and denominator are the molecular proportions of the substances in the numerator and denominator, respectively, of the "fractions" at the heads of columns under the heading "Original substances".

** A – Adipic acid; H – 1,6-hexanediamine; S – sebacic acid; T – toluene-2,4-diamine; pP – p-phenylenediamine; oP – o-phenylenediamine; mP – m-phenylenediamine.

homy products.

The original mixtures were prepared so that they contained 5, 10, 20, 40, 60, and 80% by weight of the mixture equivalent to 1,6-hexanediamine adipate or sebacate. The polycondensation was carried out for six hours at 250°. The melting points of the products are given in Table 3.

TABLE 3

Melting Points of Four-Component Mixed Polyamides Containing an Aromatic Component

Ratio of original substances ••	Original substances •			
	AmP / P_1	SmP / P_1	AmP / P_2	SmP / P_2
1.0/0.0	258-259	145-150	258-259	145-150
0.8/0.2	130-136	95-100	130-137	100-104
0.6/0.4	96-104	78-85	110-114	85-92
0.4/0.6	90-96	70-76	105-108	80-86
0.2/0.8	105-110	88-93	130-136	90-97
0.1/0.9	125-130	105-110	145-150	115-121
0.05/0.95	155-160	–	–	120-125
0.0/1.0	145-147	145-147	160-162	160-162

The products were yellow solids. Their solubilities were lower than those of the original mixed polyamides P_1 and P_2; thus, a 15% alcoholic solution of the polyamide P_1 did not gel after 24 hours, whereas a 10% solution of the product containing only 10% of "m-phenylenediamine adipate" gelled as soon as it was cold. As Fig. 1 shows, the solubility falls regularly as the m-phenylenediamine content rises. Polyamides containing more than 60% of the m-phenylenediamine salt are no longer soluble in alcohol. All these products are somewhat more soluble in a mixture of ethanol and chloroform, but again the solubility falls as the m-phenylenediamine content rises, and it finally approaches zero. These polyamides are more readily soluble in cresol, and, whereas heat must be applied in order to dissolve them in alcohol, they are already soluble in the cold in cresol. However, with increase in the m-phenylenediamine content, the solubility again falls.

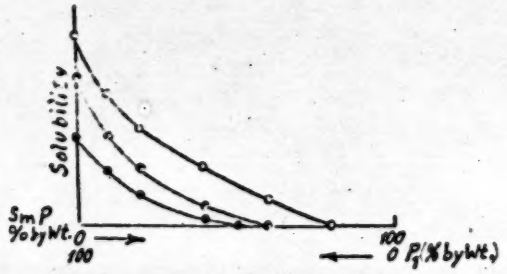


Fig. 1. Relative solubilities in various solvents of mixed polyamides of the system P_1 – SmP: o – mixture of ethanol and chloroform; ● – ethanol; ● – methoxyethanol

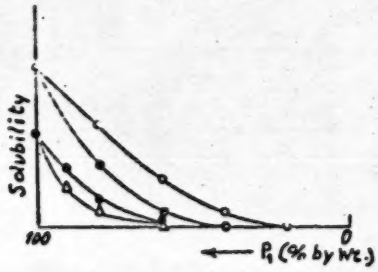


Fig. 2. Dependence of the solubilities of polyamides of various systems in ethanol on the content of the aromatic component: o – P_1 + SmP; ● – P_1 + AmP; ● – P_2 + SmP; Δ – P_2 + AmP

The solvents may be placed in the following order of diminishing solvent power: cresol, 2 : 1 mixture of ethanol and chloroform, ethanol, 2-methoxyethanol, 2-ethoxyethanol. These polymers are insoluble in chloroform, cyclohexanone, and benzene. Fig. 1 shows the dependence of the solubility of polyamides of the system P_1 – SmP (in ethanol, in a mixture of ethanol and chloroform, and in 2-methoxyethanol) on the m-phenylenediamine content. Polyamides into which m-phenylenediamine was introduced in association with sebacic acid are somewhat more soluble than those in which the diamine was associated with adipic acid (Fig. 2).

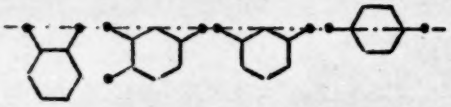
• P_1 – a mixture of AH (40%), SH (20%), and 6-caprolactam (40%); P_2 – a mixture of AH (40%), SH (40%), and 6-caprolactam (20%).

•• The numerator and denominator are the proportions by weight of the substances in the numerator and denominator, respectively, of the "fractions" at the heads of columns under the heading "Original substances".

DISCUSSION OF RESULTS

The various series of mixed polyamides that we prepared from components that include an aromatic diamine show points of resemblance to the previously described purely aliphatic polyamides. Thus, mixed polyamides having aromatic components generally have lower melting points than the corresponding single-component polyamides, as can be seen from Figures 3, 4, and 5, in which the dependence of melting point on composition is given for the systems AH−AmP, AH−AoP, AH−AmP, AH−AT, AH−SmP, SH−SmP. The same can be seen also from Figures 6 and 7, in which the dependence of melting point on the ratio of the amount of the m-phenylenediamine salt to the total amount of the remaining three components is given for the systems P_1−AmP, P_1−SmP, P_2−AmP, P_2−SmP.

With increase in the content of aromatic component the melting point of the polyamide gradually falls, passes through a minimum at a definite content of this component, and then rises again. The minimum melting point is found at different compositions in different systems, and no definite law could be found. The cause of this is evidently to be found in the different structures of the original aromatic diamines. The greatest lowering of melting point is given by o-phenylenediamine, and toluene-2,4-diamine, m-phenylenediamine, and p-phenylenediamine follow in order of reducing effect. This is to be associated, of course, with the differences in structure of these diamines.



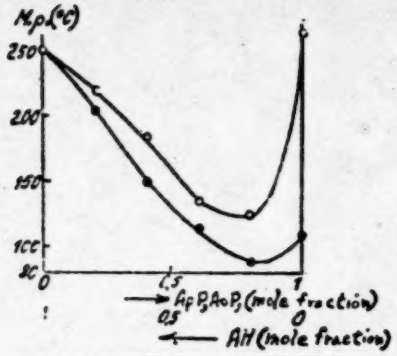


Fig. 3. Dependence of the melting points of polyamides on the proportions of reactants: o−AH−ApP; •−AH−AoP

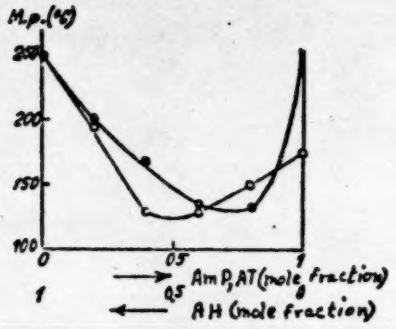


Fig 4. Dependence of the melting points of polyamides on the proportions of reactants: •-AH−AmP; o-AH−AT.

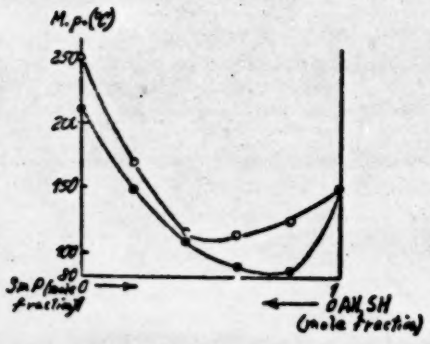


Fig. 5. Dependence of the melting points of polyamides on the proportions of reactants: o- AH−SmP; •-SH−SmP

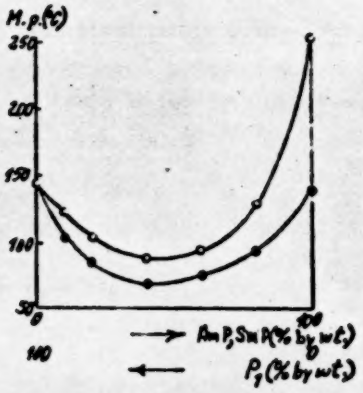


Fig. 6. Dependence of the melting points of polyamides on the contents of m-phenylenediamine adipate and of m-phenylenediamine sebacate: o-P_1−AmP; •-P_1−SmP

The aromatic system in o-phenylenediamine, and to a lesser extent in m-phenylenediamine and in toluene-2,4-diamine, hinders the mutual approach of the polymer chains and makes it difficult for them to take up an ordered arrangement, so that the melting point is lowered. In toluene-2,4-diamine the volume of the aromatic system is increased owing to the presence of the methyl group. Unlike the purely aliphatic systems, all the investigated systems having aromatic components show no correlation between solubility and melting point. It is possible that this is associated with the formation of cross links and transformation into three-dimensional polymers.

The introduction of aromati nuclei into a polyamide molecule generally yields products of appreciably higher melting point than the corresponding purely aliphatic polyamides. Table 4 gives the melting points of polyamides formed by sebacic acid with aromatic and aliphatic diamines having equal numbers of carbon atoms in the chain.

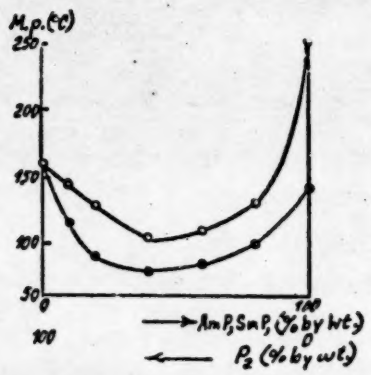


Fig. 7. Dependence of the melting points of polyamides on the contents of m-phenylenediamine adipate and of m-phenylenediamine sebacate: o- P_2—AmP; ●-P_2—SmP

TABLE 4

Melting Points of some Polyamides of Sebacic Acid

Diamine	M.p. (°C)	Literature reference
Benzidine	375	7
1,8-Octanediamine	197	8
α,α'-Bi-p-toluidine	360	9
1,10-Decanediamine	194	8

A similar result is obtained when the aromatic nucleus is a part of the structure of the acid, as can be seen by comparing the melting point of polyhexamethyleneterephthalamide (400° [10]) with that of polyhexamethyleneadipamide (250°).

SUMMARY

1. Mixed polyamides were prepared from an aromatic diamine (toluene-2,4-diamine, o-phenylenediamine, m-phenylenediamine, or p-phenylenediamine), 1,6-hexanediamine, and a dicarboxylic acid (adipic or sebacic), and also from m-phenylenediamine, 1,6-hexanediamine, 6-caprolactam, and adipic and sebacic acids.

2. The dependence of the melting points and solubilities of the polymers on the composition of the original mixture was determined. It was found that the melting point of a mixed polymer passes through a minimum.

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No.1, 163.*

[2] V. V. Korshak and T. N. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No.2, 372.**

[3] S. A. Mahood, P. V. L. Schaffner, Org. Synth. 11, 32 (1931).

[4] N. V. Sidgwick, J. A. Neill, J. Am. Chem. Soc. 123, 2813 (1923).

[5] Ch. A. Kraus, G. F. White, J. Am. Chem. Soc. 45, 774 (1923).

[6] Callam, Henderson, J. Soc. Chem. Ind. 38, 409 (1919).

[7] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 974 (1944).

[8] D. D. Coffman, G. J. Berchet, W. R. Peterson, E. W. Spanagel, J. Polymer Science 2, 306 (1947).

[9] V. V. Korshak and S. V. Rogozhin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No 5, 593.

* See Consultants Bureau Translatich, p. 145.
** " " " " p. 333.

[10] O. B. Edgar, R. Hill, J. Polymer Science, 8, 1 (1952).

[11] V. V. Korshak, T. M. Frunze, Proc. Acad. Sci. USSR, 97, 261 (1954).

MACROMOLECULAR COMPOUNDS

COMMUNICATION 75. DEPENDENCE OF THE PROPERTIES OF POLYAMIDES ON THE EXTENT OF INTERMOLECULAR HYDROGEN BONDING

V. V. Korshak and T. M. Frunze

We have previously described binary mixed polyamides derived from the salts formed by 1,6-hexanediamine with two different dicarboxylic acids [1], from 6-caprolactam and the 1,6-hexanediamine salt of a dicarboxylic acid [2], and from the salts of an aromatic diamine and 1,6-hexanediamine with various dicarboxylic acids; we have studied these with the object of determining the effect of the extent of hydrogen bonding on the properties of the polyamides. In order to throw further light on the effect of this factor on the properties of polyamide systems derived from three and four original components, we have prepared mixed polyamides from the following reactants, taken in various proportions: the 1,6-hexanediamine salts of succinic, adipic, azelaic, and sebacic acids, and 6-caprolactam (2-oxohexamethylenimine).

EXPERIMENTAL

Descriptions have already been given of the purification of the starting materials and their properties [1-3], and also of the methods of performing the polycondensation reaction and of determining the properties of the products [1]. One of the systems investigated (AdH–SebH–C) has been studied also by Catlin, Czerwin, and Willey [4]. Our results for this system are in complete accord with the results obtained by these authors.

In the systems that we investigated we prepared polyamides from various proportions of reactants, and we characterized these products as in previous investigations: we determined the molecular weight, the solubility in various solvents, and the melting point. After polycondensation for six hours the molecular weights of the products were in the region of 17,000. White horny products were obtained which were sometimes quite transparent and extremely strong. They all gave fibers and films from the melt, and these could be cold-drawn; some of them gave transparent films from solution.

The solubilities of polyamides of this group are greatly dependent on composition and are generally higher than those of the products described previously. Their melting points are as high as, or even higher than, those of the binary products. It is evident that, when comparisons are made between systems of mixed polyamides differing in the number and kinds (aliphatic or aromatic) of component reactants, it is no longer possible to draw an exact parallel between melting point and solubility, as we have done previously [1,2].

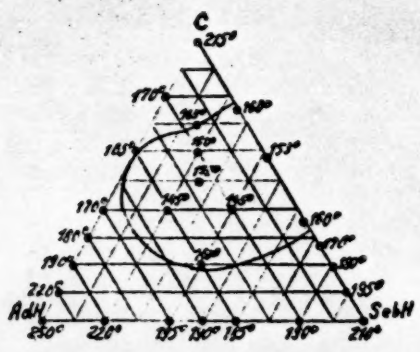


Figure 1. Variation of the melting points of polyamides of the system AdH–SebH–C; —— m.p. 165°.

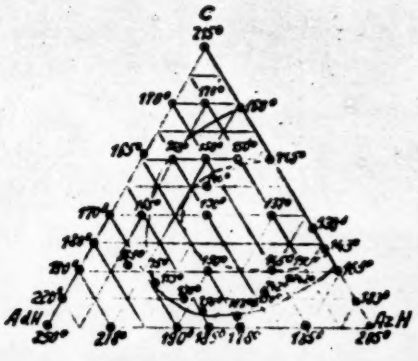


Figure 2. Variation of the melting points of polyamides of the system AdH–AzH–C; ——m.p. 160° --- m.p. 145°

TABLE 1

Dependence of the Melting Point of a Mixed Polyamide Prepared from 1,6-Hexanediamine Salts of Dicarboxylic Acids on the Proportions of Reactants

AdH – AzH – SebH	AdH – AzH – SebH	AdH – AzH – SebH	SucH – AdH – SebH	SucH – AdH – AzH
200-204°	158-161°	155-161°	200-206°	190-195°
60-20-20	25-50-25	17-51-32	43-0-57	44-0-56
172-176°	180-183°	165-170°	190-195°	167-173°
40-20-40	10-60-30	36-53-11	43-10-47	44-10-46
175-179°	190-193°	165-167°	180-186°	165-170°
20-20-60	10-80-10	30-34-36	44-20-36	45-20-35
190-195°	170-175°	165-167°	180-184°	170-175°
50-40-10	46-21-33	33(3)-33(3)-33(3)	44-30-26	45-31-24
165-174°	170-174°	180-184°	190-195°	
30-40-30	17-30-53	46-43-11	36-52-12	
162-166°	175-179°	175-178°	205-210°	
30-60-10	36-10-54	46-32-22	47-53-0	
170-174°	165-170°	180-184°		
20-60-20	9-50-41	45-11-44		

1. Abbreviations: H – 1,6-hexanediamine, Ad – adipic acid, Az – azelaic acid, Seb – sebacic acid, Suc – succinic acid.

2. The numerators of the "fractions" are the melting points of the polyamides. The denominator of a "fraction" gives the relative amounts (as percentages) of the reactants in the order in which they are given at the top of the column.

TABLE 2

Dependence of the Melting Point of a Mixed Polyamide Prepared from 6-Caprolactam on the Proportions of Reactants*

AdH – AzH – C	AdH – AzH – C	AdH – SebH – C	AdH – SebH – C	AdH – AzH – SebH – C
175-178°	150-155°	158-162°	160-165°	120-125°
60-20-20	12-68-20	20-60-20	40-40-20	26-30-32-12
145-148°	142-147°	145-148°	145-148°	140-144°
40-40-20	22-64-14	40-40-20	40-20-40	20-47-24-9
140-144°	142-147°	145-149°	145-150°	140-143°
20-60-20	26-62-12	60-20-20	20-40-40	19-43-20-18
165-169°	150-155°	115-118°	155-160°	145-150°
50-10-40	31-60-9	10-50-40	25-25-50	31-36-19-14
130-133°	168-172°	130-134°	160-164°	130-134°
30-30-40	39-57-4	30-30-40	20-20-60	17-40-21-22
137-140°	180-190°	110-113°	165-170°	148-150°
10-50-40	70-0-30	50-10-40	15-15-70	29-34-18-19
158-162°	176-170°	120-125°		110-115°
30-10-60	63-15-22	10-30-60		19-23-24-34
155-158°	155-160°	140-144°		110-115°
20-20-60	58-27-15	20-20-60		25-25-25-25
140-143°	150-155°	115-119		125-130°
25-25-50	53-37-10	25-25-50		17-19-20-44
150-154°	150-155°	140-143°		145-152°
10-30-60	49-46-5	30-10-60		26-15-15-44
175-178°	185-195°	170-174°		
10-10-80	46-54-0	10-10-80		

*C denotes 6-caprolactam. Other abbreviations are as in Table 1.

The melting points of the products obtained are given in Tables 1 and 2.

DISCUSSION OF RESULTS

Ternary diagrams showing the dependence of melting point on composition for mixed polyamides are given in Figures 1, 2, 3, and 4 for the systems AdH – SebH – C, AdH – AzH – C, AdH – AzH – SebH, and AzH – SebH – C. It will be readily seen that the polyamides of lowest melting point lie nearest to the center of the triangle. If, however, a particular component predominates, the polyamide is further from the center of the triangle and has a higher melting point. Constant melting point isotherms are displaced in the direction of the side of the triangle representing the system having the lowest melting points. It is clear that in ternary systems the derangement of structure and the obstacles in the way of hydrogen bonding are still greater than in the binary systems studied previously [1, 2, 3].

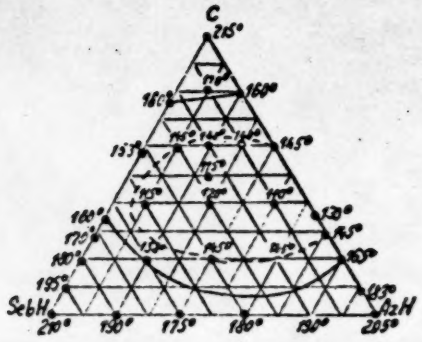


Figure 3. Variation of the melting points of polyamides of the system AzH – SebH C; ———— m.p. 160°; ------- m.p. 145°.

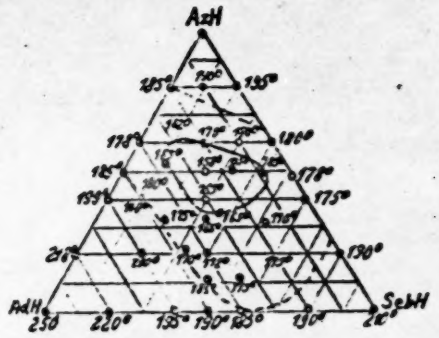


Figure 4. Variation of the melting points of polyamides of the system AdH – AzH – SebH; ———— m.p. 165° --------m.p. 185°.

When we consider the possibilities of hydrogen bonding in the system AdH – SebH – C (1 : 1 : 1) for the following three chain structures:

– Ad – H – Seb-H — C — Ad — H — Seb - H — C —

– Seb - H – Ad–H — C — Seb – H —Ad — H — C —

– C — Ad –H –Seb - H — Ad— H —Seb – H — C —

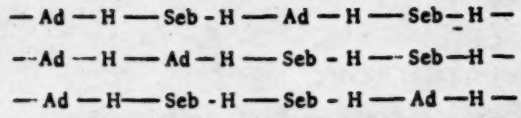
we find that the hydrogen bonds formed are as indicated by the dotted lines in the following scheme, in which the number of main-chain atoms in each monomer unit is expressed by a figure:

– 6 – 8 – 10 – 8 – 7 – 6 – 8 – 10 – 8 – 7 –

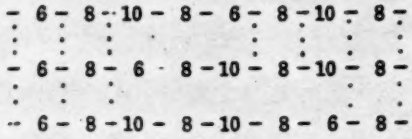
– 10 – 8 – 6 – 8 – 7 – 10 – 8 – 6 – 8 – 7 –

– 7 – 6 – 8 – 10 – 8 – 6 – 8 – 10 – 8 – 7 –

On the other hand, considering the binary system AdH – SebH for the following chain structures:



we find that the hydrogen bonding will be as indicated in the following scheme:



It is evident that in the second polymer the proportion of amide groupings that participate in intermolecular hydrogen bonding will be considerably greater than in the first.

We have already shown [1] that there is a linear relationship, $y = 7x + 110$, between the melting point of a polyamide and the extent of hydrogen bonding (y is the melting point and x is the mole percentage of hydrogen bonds) [1, 5]. In Table 3 we give figures, calculated with the aid of this equation, which provide a measure of the extent of hydrogen bonding in the ternary polyamide systems that we have investigated.

TABLE 3

Dependence of the Proportion of Hydrogen and Amide Linkages present in Polyamides on Composition

Composition of the polyamide	Molar proportions of components	M.p. (°C)	Proportion of hydrogen bonds (%)	Proportion of amide linkages (%)	Proportion of the amide linkages that are hydrogen-bonded (%)
AdH	–	250-252	20.0	20.0	100.0
AzH	–	205-207	13.6	15.4	88.3
SebH	–	210-212	14.3	14.3	100.0
C	–	215-217	15.0	20.0	75.0
AdH – SebH	2 : 3	185-187	10.7	16.1	66.4
AdH – AzH	2 : 3	178-180	9.7	16.9	57.4
AzH – SebH	2 : 3	170-173	8.5	14.7	57.7
AzH – C	2 : 3	130-132	3.0	17.0	17.6
SebH – C	1 : 4	153-155	6.1	17.6	34.6
AdH – AzH – C	1.1 : 1 : 3.56	130-123	2.8	19.0	14.7
AdH – SebH – C	1 : 1.6 : 4.6	145-150	5.0	17.6	28.4
AdH – SebH – C	2.4 : 1 : 5.6	145-148	5.0	18.6	27.4
AdH – SebH – C	1.2 : 1 : 1.3	160-162	7.1	17.5	40.5
AdH – SebH – C	1.1 : 1 : 1 : 8.4	160-164	7.1	18.1	39.2

It can be seen from Table 3 that a considerable proportion of the amide groupings present in mixed polyamides is not linked by hydrogen bonds to the amide groupings of neighboring macromolecules. Such amide groupings have no effect on the melting point and other properties of the mixed polyamides. Confirmation of this inference can be found in the fact that the melting points of polyamides derived from 1,6-hexanediamine and dicarboxylic acids having odd numbers of carbon atoms in their molecules do not fall on the graph when it is assumed that all their amide groupings are hydrogen-bonded. Owing to the operation of steric factors, hydrogen bonds can be formed by only a part of the amide groupings of such polyamides, thus accounting for the observed discrepancy.

The results now obtained also confirm another of the conclusions reached in our earlier work [1], namely, that no polyamide derived from straight-chain aliphatic diamines and dicarboxylic acids, and having no alkyl side groups, other substituents, or hetero atoms, can have a melting point below that of polyethylene, i.e., 110°. The results provide further new material confirming the correctness of a conclusion that we reached previously, namely, that there is a direct relationship between the melting points of mixed polyamides and the extent to which hydrogen bonding occurs in these polymers.

SUMMARY

1. An investigation was made of the dependence of the melting points of ternary and quaternary polyamides on their quantitative composition, the reactants in the systems studied being the 1,6-hexanediamine salts of succinic, adipic, azelaic, and sebacic acids and 6-caprolactam, taken in various proportions.

2. The extent to which hydrogen bonding occurs in these polymers was calculated.

3. It was proved that the melting points of mixed polyamides derived from straight-chain aliphatic diamines and dicarboxylic acids and not containing side chains, substituents, or hetero atoms cannot be below the melting point of polyethylene.

Received April 14, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 163. *

[2] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 372. **

[3] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 3, 551. ***

[4] W. E. Calin, E. P. Czerwin, R. H. Willey, J. Polymer Science, 2, 412 (1947).

[5] V. V. Korshak and T. M. Frunze, Proc. Acad. Sci. USSR, 97, 261 (1954).

---

* See Consultants Bureau Translation, p. 143.

** " " " " p. 333.

*** " " " " p. 487 this issue.

BLANK
PAGE

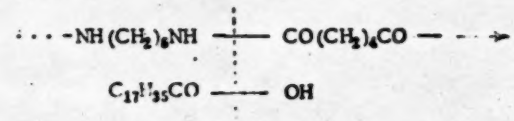
MACROMOLECULAR COMPOUNDS

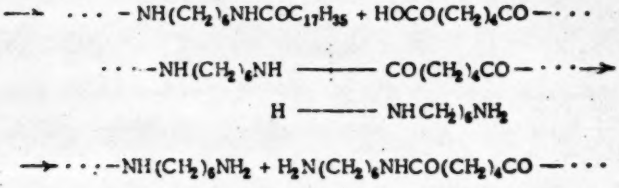
COMMUNICATION 76. ROLE OF EXCHANGE REACTIONS IN POLYAMIDE FORMATION

V. V. Korshak and T. M. Frunze

It was shown long ago by one of us in collaboration with Rafikov [1], Pinkina [2], and Zamyatina [3] that exchange reactions occur between polyamide macromolecules and the substances of low molecular weight from which they are prepared, such as mono- and di-carboxylic acids and diamines. Such exchange reactions are degradative, and they result in the breakdown of the polyamide macromolecule, either by acidolysis — by reaction with a dicarboxylic acid — or by aminolysis — by reaction with a diamine. The regularities to be observed in these reactions were studied by one of us in collaboration with Zamyatina [3], the example taken being polyhexamethyleneadipamide, which was subjected to acidolysis by adipic and stearic acids and to aminolysis by 1,6-hexanediamine.

Acidolysis and aminolysis are reactions in which the active carboxyl or amino group of the acid or amine taken reacts with the amide grouping of the polymer in the following manner:





It was found that the extent to which the polyamide was degraded was proportional to the amount of acid or amine used.

The investigation of several different polyamide systems has shown that amidolysis exchange reactions can occur between amide groupings [13, 14], and one of us in collaboration with Vinogradova [4,5], and also with Kursanov and Vinogradova [6], has shown that a similar, esterolysis exchange reaction can occur between two ester groupings, both in polyesters and in esters of low molecular weight.

The important part played by exchange reactions in the process of polyamide formation is evidenced also by the results of an investigation of the reaction between 2-aminoethanol and sebacic acid carried out by one of us in collaboration with Chelnokova and Distler [7]. It was shown that in the course of the formation of the polyamidoester extensive rearrangement of the monomer units of the macromolecule occurred.

It was shown by one of us in collaboration with Bresler, Pavlova, and Finogenov [8] that the interaction of two polyamide fractions of different molecular weights yields a polyamide whose molecular weight is between those of the original fractions, which proves that a state of polycondensational equilibrium is attained in reactions between polyamide macromolecules. However, prior to the present investigation we had not obtained direct proof of the occurrence of such exchange reactions between polyamide macromolecules as could bring about a considerable measure of exchange of monomer units between the macromolecules and the "leveling out" of their compositions. The investigation of such reactions is of great interest for the correct understanding of the mechanism of polyamide formation and polycondensation processes in general.

In order to investigate the course and extent of such reactions we studied the behavior of polyamides of different structures when heated together in the molten condition. For this purpose we prepared two single-component

polyamides – from 1,6-hexanediamine azelaate and 1,6-hexanediamine sebacate. Polyhexamethyleneazelaamide melted at 205° and was completely insoluble in ethanol and in 2-methoxyethanol. Polyhexamethylenesebacamide melted at 210° and was also insoluble in ethanol and 2-methoxyethanol.

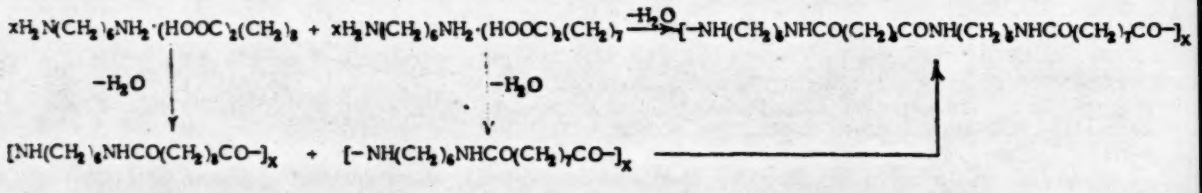
We first determined the mutual solubilities of the molten polyamides. Bematskaya and Kudryavstev [9] showed that polycaprolactam and polyhexamethyleneadipamide are miscible in all proportions, and it could be expected that our polyamides would behave in the same way. Mixtures of these polyamides were stirred at 250° in an atmosphere of nitrogen. It was found that they formed a homogeneous mixture in all proportions; the product was insoluble in alcohol.

A mixture obtained by melting two molecular proportions of polyhexamethyleneazelaamide with three molecular proportions of polyhexamethylenesebacamide was heated for 24 hours in cresol solution, at first at 150-180°, and for the last eight hours at 240°. The resulting polyamide melted at 180-183° and dissolved when heated with ethanol or 2-methoxyethanol. The same mixed polyamide was obtained when 15 g of polyhexamethyleneazelaamide was heated with 23.6 g of polyhexamethylenesebacamide at 240-250° in an atmosphere of nitrogen in an autoclave for 30 hours. It melted at 178-183° and dissolved when heated with ethanol or 2-methoxyethanol. A mixed polyamide of the same composition was obtained from 0.4 mole of 1,6-hexanediamine azelaate (AzH) and 0.6 mole of 1,6-hexanediamine sebacate (SH). It melted at 170-175° and dissolved when heated with ethanol or 2-methoxyethanol, i.e., was the same product as that obtained by heating the polyamides themselves. The somewhat higher melting points of the first products are evidently to be explained by incomplete attainment of equilibrium as a result of the high viscosity of the melt of the original polyamide mixture.

A further object for investigation was the three-component polyamide obtained by heating a mixture of one part of polyhexamethyleneazelaamide, one part of polyhexamethyleneadipamide, and two parts of polycaprolactam at 250-260° in an atmosphere of nitrogen in an autoclave for 30 hours. The product melted at 148-153° and dissolved when heated with ethanol or 2-methoxyethanol, whereas each of the original three polyamides was insoluble in these solvents and melted above 200°. The mixture obtained by melting the above mixture of polyamides melted at 240-250° and was insoluble in ethanol and in 2-methoxyethanol. A polyamide of the same composition prepared from 1,6-hexanediamine adipate (AdH), 1,6-hexanediamine azelaate (AzH), and 6-caprolactam (1 : 1 : 2) melted at 140-143° and dissolved when heated with ethanol or 2-methoxyethanol, i.e., was the same product as that obtained by heating the polyamides themselves and was greatly different in properties from the mixture formed when the polyamides were melted together.

We have therefore succeeded in proving that polyamides of the same composition and properties can be prepared both directly from the appropriate monomeric substances (diamine salts of dicarboxylic acids) and by heating a mixture of polyamides, each of which is prepared beforehand from each salt separately. This statement is illustrated by the following scheme:

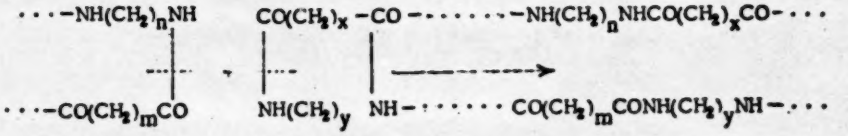
which may be expressed also by the following equations:



The results of the above-described experiments show that, when a mixture of polyamides is heated, transamidation reactions occur, so that the macromolecules of the various single-component polyamides exchange some of their repeating units with formation of new macromolecules of a mixed polyamide, all containing the same proportions of the monomer

units. It will be clear that such a result could be obtained only by the occurrence of exchange reactions between separate polyamide molecules, and the fact that this result is obtained provides a reliable proof of the occurrence of such reactions.

These exchange reactions between macromolecules contribute to the polycondensation equilibrium, and it is evident that they occur both with the end groups of the macromolecules by the acidolysis or aminolysis mechanism (see above), and also by interaction of the amide groupings of different macromolecules by the amidolysis mechanism, as follows:



We may note, incidentally, that such a leveling out of composition is very probable from the thermodynamical point of view, since random distribution of monomer units should lead to increase of entropy.

We must draw attention to another important conclusion that can be drawn from the results, namely, that it is now clear that the structure and composition of the macromolecules of mixed polyamides, and probably also polyesters, are determined in the final stage not by the kinetics of the individual elementary processes, as in the copolymerization of vinyl monomers, but by polycondensation equilibrium, which depends on the proportions of the separate monomeric reactants. This conclusion lends further emphasis to the fundamental difference that exists – in reaction mechanism, and in the laws governing the reaction – between polymerization and polycondensation processes, a fact that we have frequently pointed out in the past [10-12].

SUMMARY

1. When mixtures of different single-component polyamides were heated, mixed polyamides were formed, and these were similar to the products obtained when the appropriate mixtures of monomers were heated.

2. It was shown that exchange reactions play an important part in polycondensation processes.

3. It is considered that the structure and composition of polyamide macromolecules, and also their fractional composition, are determined not by the kinetics of the individual stages of the process, but by the state of polycondensation equilibrium.

Received April 14, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 974 (1944); Proc. Acad. Sci. USSR 48, 36 (1945).

[2] S. R. Rafikov, V. V. Korshak, and L. N. Pinkina, J. Gen. Chem. 14, 1003 (1944).

[3] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, 609.

[4] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 1109.*

[5] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 334.

[6] D. N. Kursanov, V. V. Korshak, and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 140. **

[7] V. V. Korshak, G. N. Chelnokova, and G. I. Distler, Proc. Acad. Sci. USSR, 82, 589 (1952).

[8] S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Fincgenov, Proc. Acad. Sci. USSR, 87, 961 (1952).

* See Consultants Bureau Translation, p. 967. ** See Consultants Bureau Translation, p. 125.

[9] Ya. E. Bernatskaya and G. I. Kudryavtsev, Collection of papers, "Synthetic Fibers", 3, 88 (1952).

[10] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1950, page 307.

[11] V. V. Korshak, Prog. Chem. 21, 121 (1952).

[12] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol. 1, General Methods for Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1953, p. 481.

[13] S. R. Rafikov, V. V. Korshak, and T. N. Chelnokova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 4, 743. *

[14] L. F. Beste, R. C. Houtz, J. Polymer Science 8, 395 (1952).

---

* See Consultants Bureau Translation, p. 669.

BRIEF COMMUNICATIONS

CONTACT – CATALYSIS REACTIONS OF PENTANE IN PRESENCE OF A CHROME – ALUMINA – MAGNESIA CATALYST

N. I. Shuikin, E. A. Timofeeva, and V. M. Sladkikh

In a previous investigation we have shown [1] that, as a result of the dehydrogenation of pentane over a mixed catalyst consisting of Cr_2O_3, Al_2O_3, and MgO (45 : 30 : 25 mole-%) at 500° at a space velocity of 1.2, catalyzates are obtained containing 21-22% of pentenes in admixture with some hydrocarbons of other classes, including cyclopentane.

TABLE 1

Results of the Dehydrogenation of Pentane at Various Temperatures

Results of experiment	Temperature (°C)			
	450	500	527	550
Yield of catalyzate (%)	95.0	88.5	80.4	73.9
Amount of gas evolved (liters at S.T.P.)	1.00	5.50	8.75	10.05
Properties of catalyzate:				
n_D^{20}	1.3600	1.3660	1.3675	1.3700
d_4^{20}	0.6302	0.6347	0.6368	0.6382
Iodine number	33.4	73.8	85.3	94.8
Content of unsaturateds (% by weight):	9.2	20.3	23.5	26.0
(on amount of pentane passed)	8.7	17.9	18.9	19.2
Composition of gas:				
Unsaturateds	7.1	1.2	7.3	9.1
Hydrogen	65.9	79.6	78.9	78.3
Paraffins	27.0	19.2	13.8	12.6

It was of interest to determine the effect of variation of temperature on the extent of dehydrogenation of pentane and on the composition of the catalyzate. With this object we carried out experiments on the dehydrogenation of pentane at 450-550° in presence of a chrome-alumina-magnesia catalyst. In each experiment 31.3 g of pentane was brought into contact with the catalyst at a space velocity of 1.2. The results of typical experiments are given in Table 1, which shows that with rise in temperature from 450° to 550° the content of unsaturated hydrocarbons in the catalyzate increases from 9.2% to 26%.

A combined catalyzate from experiments at 550° was fractionated through a 70-plate column. The properties of the fractions obtained are given in Table 2.

INVESTIGATION OF FRACTIONS

Fraction I. By the application of the methods of bromination and precise rectification to this fraction it was established that 2-methylbutane, unchanged pentane, pentenes (the bulk of the fraction), and 1,4-pentadiene were present.

Fraction II. Judging from the value of the iodine number, this fraction contained 26.4% of pentenes in admixture with unchanged pentane. We have checked the iodine-number method on artificial mixtures of pentane and pentenes [1].

Fraction III. Like Fraction I, this was investigated by the method of preliminary bromination, and 2.3 g of it yielded 0.2 g of unchanged pentane (b.p. 35.9-38.0°), 1.2 g of dibromopentanes (b.p. 56-62°/11 mm, n_D^{20} 1.5095 and d_4^{20} 1.6820), and 1.5 g of 1, 2, 3, 4-tetrabromopentane, m.p. 114-115° [2], which indicates that, apart from pentane and pentenes, 1,3-pentadiene (piperylene) was present in this fraction.

Fraction IV. Investigation of this fraction by the Raman-spectra method * showed that it consisted mainly of cyclopentane, a result that was fully in accord with its physicochemical properties (see Table 2). In the literature [3] the following properties are reported for cyclopentane: b.p. 49.3°, n_D^{20} 1.4068 and d_4^{20} 0.7460

TABLE 2

Properties of the Fractions of the Liquid Catalyzate Obtained in Experiments at 550°

Fraction	Boiling range (°C, corrected)	Amount (g)	Properties		
			n_D^{20}	d_4^{20}	Iodine number
I	26.5-29.0	8.2	1.3635	–	–
II	29.0-38.0	431.0	1.3635	0.6323	95.9
III	38.0-47.0	3.0	1.4140	0.6790	–
IV	47.0-52.0	2.2	1.4020	0.7410	–
V	52.0-72.5	5.0	1.3810	0.6702	26.9
VI	72.5-95.0	0.8	1.4570	–	112.3
VII	95.0-150.0	1.4	1.4845	–	44.5
VIII	150.0-200.0	1.7	1.5245	–	26.9
	Residue	1.0	–	–	–

Fraction V. After removal of unsaturated hydrocarbons by adsorption on silica gel the fraction boiled over the range 58.1-65.8° (corrected) and had n_D^{20} 1.3755 and d_4^{20} 0.6641. The presence of 2-methyl- and 3-methylpentanes was detected by the Raman-spectra method [3].

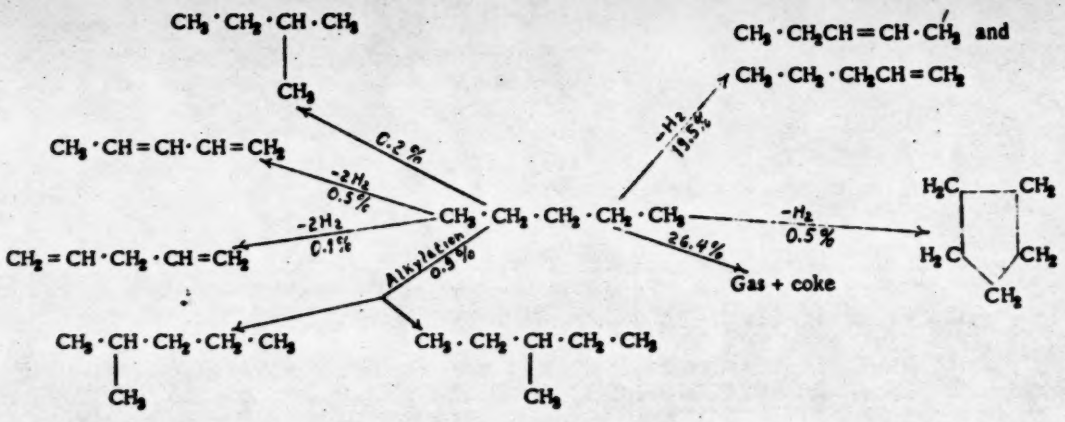
Fraction VI. Judging from the boiling range and the positive formolite test, this fraction contained benzene and other hydrocarbons.

Fraction VII. Ullmann oxidation [4] of this fraction yielded benzoic acid (m.p. 120-121°) and isophthalic acid, the dimethyl ester of which melted at 63°. We thus proved that toluene and m-xylene were present in this fraction.

In the same way the presence of m-dialkylbenzenes in Fraction VIII was established, but the identity of these could not be established in detail owing to lack of material.

The results of the investigations of the fractions isolated from the catalyzate form the basis of the following scheme of the main reactions of pentane in contact with a chrome-alumina-magnesia catalyst at 550°:

* Analysis of the fractions by the Raman-spectra method was carried out by Yu. P. Egorov, to whom we are very grateful.



We consider that benzene and its homologs were formed under our conditions as a result of the dimerization of piperylene [5], followed by redistribution of hydrogen, dehydrogenation, and dealkylation.

Thus, when the temperature of the treatment of pentane in contact with a chrome-alumina-magnesia catalyst is raised from 500° to 550°, dehydrogenation is intensified with simultaneous intensification of gas formation; small amounts of 1,3- and 1,4-pentadienes are formed.

The formation of cyclopentane by direct dehydrocyclization of pentane, which we have observed previously [1], is of fundamental interest. The formation of cyclopentane hydrocarbons as a result of the reactions of more complex paraffins – octane [6] and 2,2,4-trimethylpentane [7] – in presence of platinized charcoal (20% Pt) at 300° has been observed recently by B. A. Kazansky, A. L. Liberman, and others. We were the first to establish the possibility of the direct dehydrocyclization of pentane to cyclopentane in presence of a mixed oxide catalyst at 550°.

Received March 15, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] E. A. Timofeeva, S. S. Novikov, and N. I. Shuikin, Proc. Acad. Sci. USSR 92, No. 2, 345 (1953).

[2] A. W. Hofmann, Ber. 14, 659 (1881).

[3] G. Egloff, Physical Constants of Hydrocarbons, N. Y., Vol. 2, 1940, p. 54.

[4] F. Ullmann, J. B. Uzbachian, Ber. 36, 1797 (1903).

[5] F. Yu. Rachinsky and M. Z. Zalmanovich, Collection of Papers on General Chemistry, Volume 1, Acad. Sci. USSR Press, Moscow and Leningrad, 1953, p. 415.

[6] B. A. Kazansky, A. L. Liberman, T. F. Bulanova, V. T. Aleksanyan, and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, No. 1, 77 (1954).

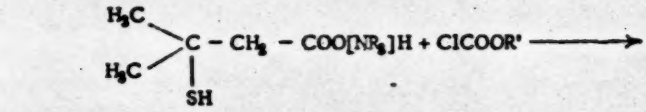
[7] B. A. Kazansky, A. L. Liberman, V. T. Aleksanyan, and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, No. 2, 281 (1954).

BLANK
PAGE

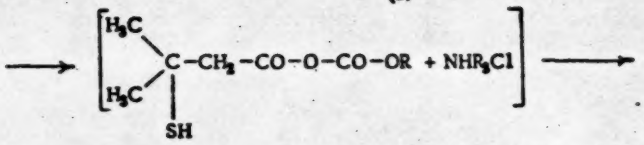
β-THIOLACTONES

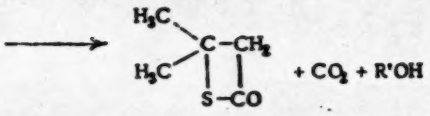
M. G. Linkova, O. V. Kildisheva, and I. L. Knunyants

The readiness with which four-membered cycles are formed has been illustrated once more by the observation we have made of the formation of thiolactones of β-mercapto carboxylic acids. Thus, when the triethylamine salt of 3-mercapto-3-methylbutyric acid (I) reacts with ethyl chloroformate, the thiolactone of 3-mercapto-3-methylbutyric acid (II) is readily formed:



(I)





(II)

The substance (II) is a colorless mobile liquid having a characteristic odor that is not reminiscent of the odor of thiols. This first representative of this new class of compounds – the thiolactone of 3-mercapto-3-methylbutyric acid – is an active acylating agent: it reacted with aniline, benzylamine, and valine, the respective products being the anilide and benzylamide of 3-mercapto-3-methylbutyric acid and N-(3-mercapto-3-methylbutyryl) valine. The hydrolysis of the thiolactone of 3-mercapto-3-methylbutyric acid with water in presence of HBr yielded the original mercapto acid. When the thiolactone was heated in a sealed tube with traces of moisture, a solid linear polymer was obtained.

EXPERIMENTAL

1. A solution of 4.6 g of ethyl chloroformate in 10 ml of chloroform was added at −5° to a mixture of 5 g of the substance (I), 40 ml of chloroform, and 7 ml of triethylamine. After 30 minutes the reaction for the SH group was negative. After addition of absolute ether (100 ml) and removal of triethylamine hydrochloride (6 g), the solution was washed – first with water, then with sodium bicarbonate solution, and finally with water again – and dried with sodium sulfate. The residue after removal of solvents boiled at 33-34° (1.5 mm) and consisted of 2 g (50%) of the thiolactone of 3-mercapto-3-methylbutyric acid, d_{20}^{20} 1.0425; n_D^{20} 1.4865; Calculated MR 31.23; Found MR 31.9; M 109 (cryoscopically in benzene).

	Found %:	C 51.81; H 6.99; S 27.01
C_5H_8OS.	Calculated %:	C 51.72; H 6.9; S 27.58

Anilide – obtained in the form of needles (from heptane), m.p. 78-79°.

	Found %:	N 6.8
$C_{11}H_{13}ONS$.	Calculated %:	N 6.7

Benzylamide – needles (from heptane), m.p. 61-62°.

Found %: C 64.23; H 7.81; S 14.39; N 6.03
$C_{12}H_{17}ONS$. Calculated %: C 64.57; H 7.62; S 14.35; N 6.27

2. The thiolactone of 3-mercapto-3-methylbutyric acid (0.22 g) was added to a vigorously stirred solution of 0.22 g of the sodium salt of valine in 30 ml of water. After 90 minutes the solution was acidified to Congo red and filtered. The product was 0.2 g of N–(3-mercapto-3-methylbutyryl) valine in the form of colorless crystals, m.p. 122-123° (from benzene or ethyl acetate).

Found %: C 51.40; H 8.13; S 13.92; N 5.90
$C_{10}H_{19}O_3NS$. Calculated %: C 51.5; H 8.15; S 13.73; N 6.00

Received April 4, 1955

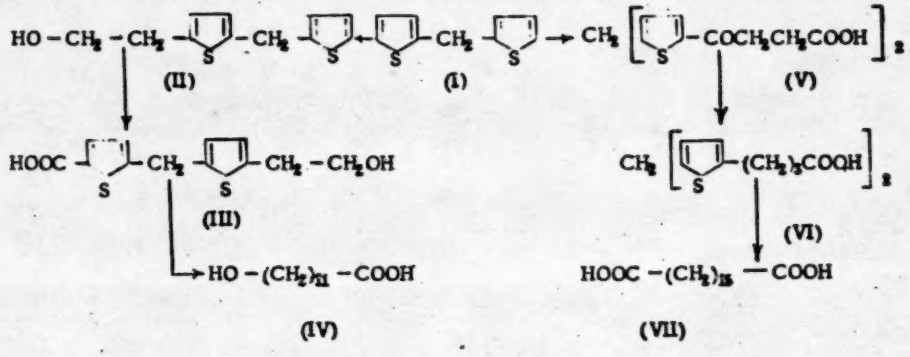
Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

SYNTHESIS AND REACTIONS OF SOME 2,2'-METHYLENEDITHIOPHENE DERIVATIVES

Ya. L. Goldfarb and M. L. Kirmalova

Since 1952 one of us has been working on the hydrogenolysis of substituted thiophenes with formation of aliphatic compounds [1]. By this method we have prepared some difficultly accessible hydrocarbons, higher aliphatic alcohols, ketones, and amino acids. One of our starting materials was 2,2'-methylenedithiophene (I), from which we prepared 1,13-tridecanediol, undecyl alcohol, and decanoic acid. We also studied the preparation of aliphatic hydroxy acids and dicarboxylic acids. This part of the investigation of the hydrogenolysis of thiophene derivatives is not yet complete, but the appearance of papers by Badger and coworkers [2] and by Buu-Hoi and Dat Xuong [3] has prompted us to publish some of our results.

When 5-thenyl-2-thiopheneethanol (II) is treated with two molecular proportions of butyllithium, the α-hydrogen of the former is replaced, the second molecular proportion of butyllithium being required for the formation of the O-lithium derivative. When an ether suspension of the product is mixed with solid carbon dioxide, 5-[(2-hydroxyethyl)thenyl]-2-thiophenecarboxylic acid (III) is formed in a yield of about 32%. Hydrogenolysis of this substance in presence of Raney nickel gives 12-hydroxydodecanoic acid (IV) in high yield.



Acylation of (I) with succinic anhydride in nitrobenzene in presence of aluminum chloride, or with the acid chloride of the monomethyl ester of succinic acid in benzene or heptane in presence of stannic chloride, yields 3,3'-(5,5'-methylenedithenoyl)dipropionic acid (V) (29% and 47% yield, respectively). The crude acid is very much contaminated with resin, and this is difficult to remove. The best method of purification is crystallization from water, but owing to the low solubility of the acid it is necessary to work with very large volumes or to carry out long extractions in a Soxhlet. After separation from aqueous solution, the acid requires still further purification.

By reduction of the acid (V) by a modification of Kizhner's method [4], we obtained 5,5'-methylenedi-2-thiophenebutyric acid (VI), and hydrogenolysis of this yielded heptadecanedioic acid (VII). We were unable to isolate this acid from the reaction mixture in the usual way, because it was strongly adsorbed by the catalyst. The catalyst was therefore dissolved in excess of hydrochloric acid, and the acid (VII) was extracted from the resulting mixture with ether. It is probable that only part of the acid formed passed into the ether, for, after purification it was found to be insoluble, not only in ether, but also in benzene, chloroform, etc.

EXPERIMENTAL

Preparation and Hydrogenolysis of the Acid (III)

1. A solution of 0.03 mole of butyllithium in ether was added at −5° to 0° to a solution of 0.015 mole (3.5 g) of the alcohol (II) in 30 ml of dry ether. The mixture was stirred for 15 minutes and then poured into a mixture of dry ice and ether. The precipitate then formed was dissolved in water, and the aqueous layer was separated from the ether layer and acidified, when 1.3 g (32%) of the acid (III) separated; m.p. 106.5-107.5° (from water).

After recrystallization from 50% acetic acid and then from 50% aqueous alcohol the melting point was raised to 110.5-111°. The neutralization equivalent was found to be 267.1 (calculated value 268.35).

Found %: C 53.75; 53.71; H 4.35; 4.49; S 23.81; 24.16

$C_{12}H_{12}O_3S_2$. Calculated %: C 53.71 H 4.51 S 23.90

From the ether layer 1.7 g (48%) of the substance (II) was recovered.

2. A solution of 2 g of the acid (III) in 30 ml of 10% sodium carbonate solution was mixed with 180 ml of water and with Raney nickel [5] prepared from 70 g of a 30% alloy and subsequently washed with ten successive 500-ml portions of distilled water. The mixture was stirred at 90° for 90 minutes. The catalyst was filtered off and washed with 5% sodium carbonate solution. The alkaline solution was poured into 1:1 hydrochloric acid, and 1.5 g (94%) of the acid (IV), m.p. 78-78.5°, separated. The melting point was raised to 83-83.5° by recrystallization from a mixture of ethyl acetate and petroleum ether; the literature gives 83-84° [6] and 84-85° [7]. The neutralization equivalent was found to be 216.1 (calculated value 216.3).

Found %: C 66.53; 66.78; H 11.20; 11.20

$C_{12}H_{24}O_3$. Calculated %: C 66.63; H 11.19

Preparation of the Acid (V)

A solution of 5.2 g of stannic chloride in 20 ml of benzene was added with stirring at 0° to a solution of 1.8 g of 2,2'-methylenedithiophene (I) and 3 g of the acid chloride of the monomethyl ester of succinic acid in 20 ml of dry benzene. The mixture was stirred at room temperature for four hours, and decomposition was then effected with dilute hydrochloric acid. The ester obtained was hydrolyzed when solvent was steam-distilled off. Prolonged extraction of the crude acid with water in a Soxhlet yielded 1.8 g (47.5%) of the acid (V), which melted at about 200°. After crystallization from 50% acetic acid and then from alcohol it melted with much darkening at 205-207°. The neutralization equivalent was found to be 191.1 (calculated value 190.2).

Found %: C 53.65; 53.64; H 4.18; 4.15; S 16.81; 16.71

$C_{17}H_{18}O_6S_2$. Calculated %: C 53.67; H 4.24; S 16.86

Preparation and Hydrogenolysis of the Acid (VI)

1. A mixture of 4.5 g of the acid (V), 7 ml of 100% hydrazine hydrate, and 50 ml of diethylene glycol was boiled for 15 minutes. Caustic potash (5 g) was added to the cooled solution, and the mixture was boiled for 90 minutes; water and excess of hydrazine hydrate were then distilled off. Boiling was continued for a further four hours at 180-200°, and the reaction mixture was then acidified, when 2.9 g (70%) of the acid (VI) separated. Crystallization, first from 50% acetic acid and then from 20% acetic acid, yielded 2.2 g of the acid, m.p. 106-108°. After recrystallization from water it melted at 119-119.7°. The neutralization equivalent was found to be 174.7 (calculated value 176.2).

Found %: C 57.58; 57.66; H 5.61; 5.80

$C_{17}H_{28}O_4S_2$. Calculated %: C 57.93 H 5.72

2. A mixture of 2 g of the acid (VI) in 20 ml of 10% sodium carbonate solution, 180 ml of water, and Raney nickel prepared as indicated above from 70 g of alloy was heated with stirring for about two hours at 90°. In the filtrate and in the alkaline solution obtained by washing the catalyst only traces of the required acid could be detected. The nickel was therefore dissolved in 120 ml of concentrated hydrochloric acid, and the solution was extracted four times with ether. Evaporation of the ether left 0.7 g of the acid (VII), m.p. 104-106°, raised by two crystallizations from ethyl acetate to 118-118.7°. For heptadecanedioic acid the literature [8] gives 117.5-118.6°. The neutralization equivalent was found to be 151.1 (calculated value 150.2).

Found %: C 68.04; 67.82; H 10.81; 10.61

$C_{17}H_{32}O_4$. Calculated %: C 67.96; H 10.74

LITERATURE CITED

[1] Ya. L. Goldfarb and M. S. Kondakova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 1131*; I. S. Korsakova, Thesis, Moscow, 1953; Ya. L. Goldfarb and I. S. Korsakova, Proc. Acad. Sci. USSR 96, 293 (1954); Ya. L. Goldfarb and B. P. Fabrichny, Proc. Acad. Sci. USSR 100, 461 (1955).

[2] G. M. Badger, H. I. Rodda, W.H.F. Sasse, J. Chem. Soc. 1954, 4162.

[3] N. P. Buu-Hoi, M. Sy N. Dat Xuong, Comptes rend. 240, 442 (1955).

[4] Hyang-Minlon, J. Am. Chem. Soc. 68, 2487 (1946).

[5] Organic Syntheses 4, 349, Moscow, 1953.

[6] W. H. Lycan, R. Adams, J. Am. Chem. Soc. 51, 625 (1929).

[7] P. Chuit, J. Hausser, Helv. 12, 463 (1929).

[8] A. Kreuchunas, J. Am. Chem. Soc. 75, 3239 (1953).

Received March 22, 1955

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

* See Consultants Bureau Translation, p. 993.

BLANK
PAGE

RELATION BETWEEN THE MOBILITIES OF IONS IN SOLUTION AND THEIR SELF-DIFFUSION COEFFICIENTS

O. Ya. Samoilov

According to firmly established concepts relating to the nature of the thermal movements of particles in liquids, and of ions in aqueous solutions in particular, the formation of a stream of ions in a solution under the action of an electric field results from the fact that the average number of activated jumps by ions in the direction of the field is greater than the number in the opposite direction [1]. Let φ be the work done by the field in moving an ion by a distance $\frac{l}{2}$ in the direction of the field (l is the distance between adjacent equilibrium positions of ions in the structure of the solution — the mean length of the activated jumps of the ions). The work φ is done in moving the ion from its equilibrium position to the top of the potential barrier surrounding this position. Polissar [2] made the first evaluation of the value of φ for an aqueous solution of potassium chloride, and he showed that when the field was not too great $\varphi \ll kT$ (k is Boltzmann's constant, and T is absolute temperature). When this condition is applied, the excess of the number of jumps of ions in the direction of the field over the number in the reverse direction will be [1]

$$\Delta j = \frac{1}{6} \frac{f}{kT} j\bar{l},$$

(j is the average number of jumps made by each ion in one second, and f is the force acting on the ion in the electric field — we shall assume that the field gradient is 1 V/cm). The mean velocity of ions in the direction of the field will be

$$\bar{v} = \Delta j \bar{l} = \frac{1}{6} \frac{f}{kT} j\bar{l}^2 \qquad (1)$$

The self-diffusion coefficient of the ion in solution is [1, 2]:

$$D = \frac{1}{6} j\bar{l}^2 \qquad (2)$$

It will be seen from Equations 1 and 2 that, accurate within $\overline{l^2} - \bar{l}^2$ (square of the mean square fluctuation of the value of l)

$$\bar{v} = \frac{f}{kT} D \qquad (3)$$

and for the mobility of the ions $U = \bar{v}F$ (F being the faraday):

$$U = \frac{fF}{kT} D. \qquad (4)$$

Equation 4 is Nernst's equation, being obtained by him in 1888 in a treatment of the movement of ions in solutions regarded as the movement of spheres in a continuous viscous medium. The approximate character of Equation 4 should be noted. However, since the degree of short-range order in the arrangement of particles in water and in aqueous solutions of electrolytes is probably fairly high [3], the mean square fluctuation of l may be small,

In a number of cases the translationary movement of particles in liquids must be regarded as activated jumps of two kinds [4]: jumps of isolated particles and jumps of the "cells" as a whole. This approach is extremely useful in the study of the movement of ions in solutions. In the study of self-diffusion in electrolyte solutions the question arises of whether the ion makes the activated jumps without its solvation envelope, or with it. It is clear that jumps of both kinds can occur in solutions, so that it is necessary to take both sorts of jumps into account.* It is found, however, that Equation 4 still remains valid.

Activated jumps made by an ion in association with its solvation envelope must evidently be regarded as jumps by cells. In accordance with Equation 4 we then obtain the following expression for the self-diffusion coefficient of ions in solutions:

$$D = \frac{1}{6}(j_1\bar{l}_1^2 + j_2\bar{l}_2^2). \qquad (5)$$

The subscripts 1 and 2 refer respectively to jumps by an isolated ion and jumps by a cell (an ion together with its solvation envelope).

Taking into account jumps of both kinds, we obtain for the mean velocity of the ion in the external electric field:

$$\bar{v} = \Delta j_1 \bar{l}_1 + \Delta j_2 \bar{l}_2. \qquad (6)$$

The force $\underline{f}$ exerted by the electric field on the ion is the same whether the jumps occur without the solvation envelope or with it, and the condition $\varphi \ll \frac{kT}{}$ [1, 2] is fulfilled for both kinds of jump. Hence

$$\Delta j_1 = \frac{1}{6}\frac{f}{kT} j_1 \bar{l}_1 \quad \text{and} \quad \Delta j_2 = \frac{1}{6}\frac{f}{kT} j_2 \bar{l}_2.$$

Substituting these values in Equation 6 we obtain

$$\bar{v} = \frac{1}{6}\frac{f}{kT}(j_1\bar{l}_1^2 + j_2\bar{l}_2^2). \qquad (7)$$

Comparison of Equations 5 and 7 shows that, even when the jumps of the cells as a whole are taken into account, the relations in Equations 3 and 4 are observed approximately. As the structure of dilute aqueous electrolyte solutions is very similar to that of water [3], the values of $\bar{l}_1$ and $\bar{l}_2$ are not greatly different in such solutions (they may even be regarded as equal). Hence, the accuracy of Equation 4 is the same whether or not the jumps of cells are taken into account.

Received January 12, 1955

N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences

* It is not assumed that the ion is firmly attached to any particular number of water molecules. The term "solvation envelope" refers to a definite number of constantly interchanging water molecules immediately surrounding an ion. The necessity for taking account of activated jumps made by an ion in association with such a solvation envelope is a consequence of the views that we have developed [4] on the mechanism of self-diffusion in liquids.

LITERATURE CITED

[1] K. Wirtz, Z. Naturforschung 3a, 672 (1948).

[2] Miltor J. Polissar, J. Chem. Phys. 6, 833 (1938).

[3] O. Ya. Samoilov, J. Phys. Chem. 20, 1411 (1946); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 4, 627. •

[4] O. Ya. Samoilov, Proc. Acad. Sci. USSR 101, 125 (1955).

• See Consultants Bureau Translation, p. 585

BLANK
PAGE